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CHEMICAL JOURNAL.

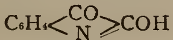
Contributions from the Chemical Laboratory of Purdue University, La Fayette, Indiana.

ON TAUTOMERIC COMPOUNDS.

By J. U. Nef.

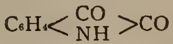
I.

There are a number of organic substances the chemical behavior of which necessitates the assumption of so-called pseudo-forms; thus, for example, carbostyril, pyridon, isátine, phloroglucin,[1] all show a twofold nature, and in order to explain this it is necessary to assume the migration of a hydrogen atom to an adjacent nitrogen or carbon atom:



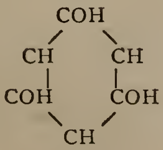
$C_6H_4 < {CO \atop N} \geqslant COH$

Isatine.

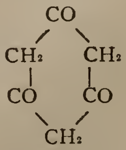


$C_6H_4 < {CO \atop NH} > CO$

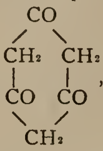
Pseudo-isatine.



Phloroglucin.



Pseudo-phloroglucin.

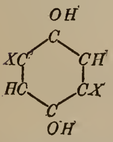
Now, as the above named compounds exist in *only one* physical modification, it is customary to explain their twofold chemical behavior as follows: it is assumed that these substances possess a so-called "mobile" or "pseudo" modification which can only be proved to exist by means of chemical reactions, and which under ordinary circumstances is incapable of existence. Thus the formation of a trioxime of phloroglucin necessitates the assumption of a pseudo-form,  , as a phenol does not react with hydroxylamine. Substances which exhibit such a twofold chemical behavior are called tautomeric.

---

[1] Von Baeyer, Ber. d. chem. Gesell. **19**, 159.

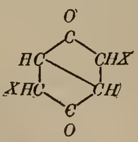
Very recently Hantzsch and Herrmann[1] have assumed the existence of tautomerism in certain so-called quinone-hydro derivatives. They base their conclusions on purely physical grounds. A number of these compounds possess a notable di- or tri-morphism. Ethyl *p*-dihydroxy-terephthalate, for example, can be obtained in three different physical modifications, and it was very natural to suppose that these modifications might correspond to chemically different molecules—that one modification corresponds to the real dihydroxy-terephthalate, while the other two might correspond to two isomeric diketo-tetrahydro-terephthalates, thus:

III



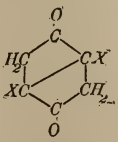
Ethyl para-dihydroxy-terephthalate (mobile modification).

I

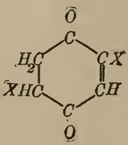


(stable modification)

II



(mobile modification)



(modification not yet discovered)

Isomeric ethyl diketo-tetrahydro-terephthalates.

Dr. W. Muthmann[2] noticed during the Easter vacation of 1887, a very remarkable dimorphism in the analogous constituted ethyl dihydroxy-pyromellithate. This substance crystallises out of pure carbon disulphide or dry ether in greenish-yellow needles (mpt. 133.2 – 133.6), and pale yellow plates (mpt. 128.5°), which can be readily separated mechanically. On dissolving either modification in ether or carbon disulphide, the mixture of the two modifications is obtained again. If these are separated and the operation repeated, the same result is invariably obtained.

---

[1] Ber. d. chem. Gesell. **20**, 1303, 2801; **21**, 1754.

[2] J. Chem. Soc. (London), **53**, 448-50.

The absorption spectrum of each modification dissolved in dilute sodium carbonate solution was quantitatively determined for all parts of the spectrum and found in both cases to be exactly the same. We had at that time, that is before the first publication of Hantzsch,[1] also the opinion that this dimorphism might be due to a difference in the molecular constitution of these substances; but since no chemical facts existed proving the ketone nature of ethyl dihydroxy-pyromellithate, we refrained from publishing our views on the subject.

It is certainly very noteworthy that hydroquinone, and also many derivatives of para-dihydroxy-benzene, are dimorphous. Dr. Muthmann has further observed that many para-diamido-derivatives of benzene are dimorphous, and especially also ethyl *p*-diamido-terephthalate.

Hantzsch and Herrmann have, in a series of papers,[2] assumed the chemical difference of the various modifications of ethyl *p*-dihydroxy-terephthalate; they assert that all para-dihydroxy or all benzene derivatives *must be* colorless, while ketones or quinones must be colored. The question of color is purely arbitrary and does not prove anything whatever. Heretofore more has been considered necessary in order to settle the constitution of a chemical compound.

Finally, the third (so-called "mobile") modification of ethyl *p*-dihydroxy-terephthalate is *not* colorless. Dr. Muthmann says on this subject: "I have obtained the third modification of this substance in large crystals (not good enough for a goniometric measurement). This modification is *not*, as Hantzsch and Herrmann assume and again and again state, *colorless*, but distinctly colored; in fact, *more intensely so* than ethyl succino-succinate (a substance which these chemists regard as colored). Prof. Lehmann[3] writes himself that the crystals show dichroism—pale green and colorless, while on the other hand he describes the succino-succinate as perfectly colorless."

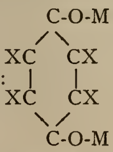
It is not necessary to take up the remarks and assumptions of Hantzsch and Herrmann one by one and to show how little they are in accordance with the actual facts. The facts presented in this paper contradict them in many respects, so that at present I am of the opinion that the peculiar dimorphism exhibited by hydroquinone derivatives is due either to a finer isomerism, such as the relative position of the atoms of the molecule in space, or to a purely physical isomerism, *i. e.* that the molecules of the substance have a peculiar tendency to arrange themselves in two (or three) definite states of equilibrium corresponding to the totally different crystalline forms.

---

[1] Ber. d. chem. Gesell. **20**, 1303.

[2] Ibid. **20**, 1303, 2801; **21**, 1754.

[3] Zeitschr. für phys. Chemie, Heft I.

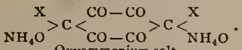
Ethyl dioxy-pyromellithate contains no double bonds, and therefore shows the characteristics of a benzene derivative. A solution of the substance in chloroform, even if allowed to stand for days, is not acted upon by an excess of bromine. The assumption of para-bonds by Hantzsch and Herrmann (see page 2, formulæ I and II) is purely arbitrary. According to the wonderful investigation of Von Baeyer on hydrated phthalic acids,[1] there is no tendency to form compounds having para-bonds. Finally, such tetrahydrated compounds, if they do exist, would surely form with bromine stable addition-products. The red-colored salts of ethyl dioxy-pyromellithate have the metal undoubtedly bound to oxygen, thus:  . The salts of this undoubted benzene-derivative are therefore *not colorless*, but deep red in color. A comparative (not yet completed) study of the salts of phenols has already shown the remarkable resemblance of these salts to one another and to the salts of ethyl aceto-acetate.

The only chemical evidence that Hantzsch and Herrmann have to offer for the tautomerism of hydroquinone compounds is the fact that ethyl tetra-oxy-terephthalate and ethyl quinone-dioxy-terephthalate form dioximes[2] with hydroxylamine. The peculiar method of formation of these substances makes it little probable that they are actually dioximes. From the experience that I have gained from the study of nitranilic acid (see following paper), there is good reason for believing that these so-called dioximes are nothing else than oxyammonium salts. The analyses of Loewy are also in favor of this conclusion. By the action of hydroxylamine chlorhydrate in excess on ethyl quinone-dioxy-terephthalate, Loewy[1] obtained a substance which he regarded as a mixture of monoxime and of dioxime, because it gave too low but constant figures on analysis:

---

[1] Ann. Chem. (Liebig) **245**, 103.

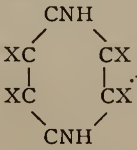
[2] Hantzsch and Zeckendorf, Ber. d. chem. Gesell. **20**, 2799, 2800.

	Calculated for  Oxyammonium salt.	Calculated for $C_6\left\{\begin{matrix}(NOH)_2\\(OH)_2\\X_2\end{matrix}\right. .$ Dioxime.
N	7.65	8.9

Loewy found 7.47, 7.58 and 7.83 per cent.

Although ethyl dioxy-pyromellithate reacts under no condition with hydroxylamine, ammonia, or ammonic acetate, it readily forms with phenylhydrazine a dipyrazolon derivative. This is, up to the present time, the only proof (chemical) that exists for the tautomerism of hydroquinone derivatives, and I do not regard it as final until the intermediary product, the dihydrazide, is isolated, as has been done in the case of ethyl succino-succinate.[2]

Experimental Part.

Ethyl quinone-di-imido-tetracarboxylate or *ethyl quinone-di-imido-pyromellithate,*  .—On adding bromine (1.8 gram dissolved in 10 grams chloroform) to a cooled solution of 2 grams ethyl diamido-pyromellithate, and allowing the mixture to stand over night, colorless needles separate out in large quantity. After allowing the chloroform to evaporate spontaneously, there remains a yellow oil, which dissolves without decomposition in alcohol, and which is either the hydrobromic acid salt or a hydrobromic acid addition-product of the above named quinone-di-imide. On adding water and rubbing with a glass rod, the oil is transformed into a solid yellow substance, while hydrobromic acid is found in the aqueous solution in large amount. On crystallising the yellow product from alcohol, it is obtained in long orange-yellow prisms, or also in radiating orange-yellow needles, melting at 161°.

---

[1] Ber. d. chem. Gesell. **19**, 2394.

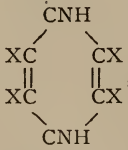
[2] Knorr, Ibid. **17**, 2055.

0.2398 gram substance dried at 110° gave 0.1257 gram H_2O and 0.4795 gram CO_2.

	Calculated for $C_6\left\{\begin{matrix}(NH)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	54.82	54.50
H	5.58	5.83

The quinone-di-imide is volatile without decomposition, and dissolves readily with pure yellow color, and without fluorescence, in chloroform, benzene, and hot alcohol. The alcoholic solution gives no coloration with ferric chloride. Zinc dust and acetic acid reduce the substance with ease to ethyl diamido-pyromellithate. The relation between these two substances is therefore similar to that which exists between quinone and hydroquinone.

The stability of the quinone-di-imide group is noteworthy; it has not been found possible in any way to convert the compound into the corresponding quinone. On dissolving it in concentrated sulphuric acid, adding a little water and heating, it remains in great part unchanged. Benzene does not extract it from a concentrated sulphuric acid solution, so that it must possess slight basic properties. Concentrated hydrochloric acid or potassium hydrate has no action on the substance. The action of concentrated nitric acid is also noteworthy. The compound dissolves therein with a dark violet color, which after a little while changes to a yellow color. On the addition of water a yellow oil is precipitated, which is insoluble in potassium hydrate, contains nitrogen, and is volatile without decomposition. This oil can in no way be converted back to the quinone-di-imide or to the diamido-compound.

In order to find out whether the quinone-di-imide possesses double bonds, , it was treated in chloroform solution with two molecules of bromine. After standing for two days, very little change was noticed. On allowing the mixture to stand for two days longer, I noticed, besides unchanged quinone-di-imide, a substance which is much more readily soluble in alcohol, and which crystallises therefrom in pale yellow large plates melting at 85°. The compound contains no bromine; it contains nitrogen, and is volatile easily without decomposition. It cannot be converted back into the quinone-di-imide or the diamido-compound. As soon as more material is at my disposal it will be thoroughly investigated. The above facts prove at all events that the quinone-di-imide contains no double bonds.

In order to obtain the material from ethyl diamido-pyromellithate for the study of the following compounds, it was found that the conversion of this substance into ethyl *p*-diketo-hexamethylene-tetracarboxylate by means of zinc dust, alcohol and dilute sulphuric acid (1 : 3), gave by far the best yield. In this way the diketo-compound was obtained mixed with 30–70 per cent. of the di-imide. The substances resemble one another very closely, are colorless, and have very nearly the same fusing point. On treating the mixture with bromine, beautiful orange-red mixed crystals (melting point 131°) of ethyl diamido- and dioxy-pyromellithate were obtained. The same mixed crystals were obtained by crystallising equal parts of these two substances from alcohol.

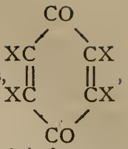
The di-imide loses its nitrogen very readily, and it is only necessary to dissolve the above mixture in concentrated sulphuric acid, to add a little water, and after standing for twenty minutes, to precipitate completely with more water. On treating the pure diketo-compound thus obtained with bromine in chloroform solution, it is converted quantitatively into ethyl dioxy-pyromellithate.

Action of Various reagents on Ethyl Quinone-tetracarboxylate.

1. *Phenylhydrazine.* On treating an alcoholic solution in the cold with phenylhydrazine, a violent evolution of gas (nitrogen) immediately takes place, and the quinone is reduced to the hydroquinone. Exactly the same reaction took place on working with an acetic acid solution.

2. *Hydroxylamine.* On adding hydroxylamine hydrochloride to an alcoholic solution in the cold, the quinone is instantly reduced to the hydroquinone. The same result is obtained with a neutral hydroxylamine solution.

3. *Ammonia.* An alcoholic ammonia solution of the quinone is reduced to the hydroquinone on warming.

4. *Bromine.* If the quinone contains double bonds,  it must form an addition-product with bromine—which it does not. One gram quinone was allowed to remain four days in chloroform solution with four molecules bromine. After the spontaneous evaporation of the chloroform (over sulphuric acid in a vacuum), there remained a product which crystallised from alcohol in greenish-yellow needles (melting point 133°), which proved to be nothing but the hydroquinone. 0.3 gram of pure hydroquinone was thus obtained; bromine therefore manifestly decomposes a part of the quinone, with the formation of the hydroquinone. If the quinone is allowed to stand in chloroform solution with bromine for a short time, one finds, besides the hydroquinone, much unchanged quinone.

These facts, as well as the observed transformation on saponification with alkalies or acids, prove the extraordinary tendency of quinone derivatives to pass over into the corresponding hydroquinone.

Action of Various Reagents on Ethyl Hydroquinone-tetracarboxylate.

1. *Hydroxylamine.* The hydroquinone dissolved in alcohol is not acted upon by hydroxylamine hydrochloride in excess, whether heated in a sealed tube at 130°–140° for six to eight hours, or allowed to stand in the cold for a week. From an alkaline solution, hydroxylamine hydrochloride precipitates the hydroquinone. This reaction will be explained clearly later. A neutral solution of hydroxylamine does not react on an alcoholic solution of the substance, whether heated in a sealed tube at 100° or allowed to stand for five days.

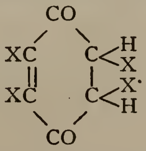
2. *Phenylhydrazine.* Although phenylhydrazine does not react in acetic acid solution, even if heated for a long time in a sealed tube at 130°, it does react very readily and completely on heating an alcoholic solution of the hydroquinone in a sealed tube at 100° for six hours. After distilling off the alcohol, the dark-brown residue was dissolved in acetic acid and precipitated in

reddish-yellow flakes by adding water. These were washed with ether, then dissolved in dilute sodium hydrate; the filtered solution thereupon poured slowly into dilute sulphuric acid, and thus the substance again precipitated in yellow flakes. For analysis it was crystallised from a large amount of pure ether, and obtained in yellow flakes.

0.0745 gram substance gave 8 cc. nitrogen at 28° and 747 mm. barom.

	Calculated for $C_6H_2\begin{cases}(CO_2C_2H_5)_2\\(N_2COC_6H_5)_2.\end{cases}$	Found.
N	11.52	11.96

The substance possesses the properties of a dipyrazolon-derivative. It dissolves in alkalies with purplish-red color and yellow fluorescence. The alcoholic solution gives with ferric chloride a dark-red coloration. It dissolves readily in alcohol, very difficultly in ether and benzene. It is soluble in concentrated sulphuric acid, and is precipitated therefrom by water in yellow flakes. On heating, it chars at a high temperature without melting. Since it can contain no unchanged CH_2 group, it gives with nitrites no pyrazol-blue[1] compound. The formation of this dipyrazolon derivative seems to prove the tautomeric nature of the hydroquinone, and we are compelled to assume the existence of a pseudo-form,



Up to the present time I have not succeeded in obtaining the dihydrazide which contains 9.5 per cent. nitrogen.

3. *Bromine.* The hydroquinone compound treated in chloroform solution with bromine in excess remains unchanged, even though allowed to stand for six days. It can therefore contain no double bonds, but reacts like a benzene derivative. The existence of a pseudo-form—a diketo-tetra-hydro-benzene compound—under ordinary circumstances is in a high degree improbable.

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[1] Knorr, Ber. d. chem. Gesells. **17**, 551, 2055.

Experiments to determine whether the Metal in the Salts of Ethyl Hydroquinone-tetracarboxylate is bound to Oxygen or to Carbon.

Isolation of the sodium salt, $C_6\begin{cases} O_2 \\ Na_2 \\ (CO_2C_2H_5)_4 \end{cases}$.—A benzene solution of ethyl hydroquinone-tetracarboxylate (1 mol.) is added slowly to a solution of 2 molecules sodium ethylate in benzene (dried over sodium). The sodium salt separates out as a gelatinous, almost invisible, red precipitate. After filtration it was put on clay plates and washed with benzene, and finally dried at 100°. It forms, thus, a deep red granular product.

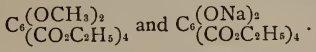
0.1374 gram substance gave 0.0445 gram sodium sulphate.

	Calculated for $C_6\begin{cases} Na_2 \\ O_2 \\ (CO_2C_2H_5)_4 \end{cases}$.	Found.
Na	10.41	10.49

When dry the salt is perfectly stable; it chars at a high temperature. An aqueous solution gives yellow flaky precipitates with barium chloride, lead acetate, and copper sulphate. A silver nitrate solution is instantly reduced in the cold. Hydroxylamine hydrochloride precipitates directly ethyl hydroquinone-tetracarboxylate, forming sodium chloride and free hydroxylamine. The dry salt brought in contact with the vapor of acetyl chloride is instantly converted, with marked evolution of heat, into sodium chloride and the diacetyl derivative of the hydroquinone which is described below. Heated with alcohol, in which it is little soluble, and methyl iodide, it is converted into sodium iodide and the dimethoxy-derivative which is described below. On adding bromine water to an aqueous solution of the salt, ethyl quinonetetracarboxylate is formed according to the equation,

$$C_6\begin{cases} Na_2 \\ O_2 \\ (CO_2C_2H_5)_4 \end{cases} + Br_2 = C_6\begin{cases} O_2 \\ (CO_2C_2H_5)_4 \end{cases} + 2NaBr.$$

This is a new method for making quinones, which promises success where other methods fail. It is not necessary to isolate the sodium salt. The hydroquinone is dissolved in the calculated amount of sodium hydrate, and the calculated amount of bromine water quickly added. Treated in this manner, ethyl dioxyterephthalate is changed: it was not possible, however, because of the small amount of substance at my disposal, to prove whether thus the long-sought-for ethyl quinone-terephthalate was actually formed. On replacing the sodium atoms in the salt of ethyl hydroquinone-tetracarboxylate with methyl, there is formed a dimethoxy-derivative which is not in the least acted upon by bromine, and which does not, under any conditions, react either with hydroxylamine or with phenylhydrazine. Thereby it is proved that the methyl groups, and hence also the sodium atoms, are bound to oxygen, as represented in these formulæ:



$$C_6\begin{matrix}(OCH_3)_2\\(CO_2C_2H_5)_4\end{matrix} \text{ and } C_6\begin{matrix}(ONa)_2\\(CO_2C_2H_5)_4\end{matrix}.$$

It is noteworthy that as soon as the metal or the hydrogen atoms in the hydroquinone are replaced by methyl or by acetyl, the products formed are perfectly colorless, show no fluorescence in solution, and give no coloration with ferric chloride. These facts are in harmony with those observed in the case of other phenols, as well as in the case of di-substituted aceto-acetic ethers.

On comparing the above reactions of ethyl disodic-hydroquinone-tetracarboxylate with those of sodium aceto-acetic ether, one cannot fail to be astonished at the great resemblance in their behavior. It is therefore also probable that in the last named compound the sodium is bound to oxygen, $CH_3-CONa=CH-CO_2C_2H_5$.

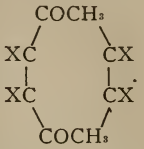
Finally, I have made the salts of a whole series of phenols, which on account of their instability have been little studied, the subject of a detailed investigation. The facts already obtained prove the great resemblance in chemical behavior of all these salts with those above mentioned. The sodium salt of hydroquinone was obtained, by means of sodium ethylate and dry ether, as a flaky white precipitate which, when moist, is extremely unstable and turns deep blue in color; when dry, however, it is tolerably stable. This salt gives reactions entirely analogous to those obtained with ethyl sodic-hydroquinone-tetracarboxylate. Hydroxylamine hydrochloride sets hydroquinone free; bromine gives quinone; acetyl chloride gives diacetyl-hydroquinone; silver nitrate is instantly reduced.

The sodium salt of tetrachlor-hydroquinone, $C_6Cl_4(\overset{1.4}{O}H)_2$, was obtained in colorless flakes which, when moist, quickly turn green. With the reagents used with hydroquinone, it gives entirely analogous reactions.

The sodium salt of resorcin, $C_6H_4(\overset{1.3}{OH})_2$, was obtained in colorless flakes. These deliquesce on heating at 100° and become viscous. The salt gives completely analogous reactions with the above reagents. Of some interest is the product, free from bromine, obtained by treating the sodium salt with bromine water.

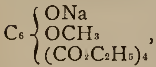
The facts which are at present known about salts which have the metal bound directly to the carbon-atom, *e. g.* the salts of the nitro-derivatives of the fatty series (Victor Meyer), show that the metal is more firmly bound and can be replaced by bromine. The silver salts are stable, and many salts are not decomposed even by mineral acids. The metal cannot be replaced by the methyl or acetyl group.

Ethyl Dimethoxy-hydroquinone-tetracarboxylate,



This compound is formed by treating the sodium salt with methyl iodide. It was made, just as in the case of the alkyl derivatives of aceto-acetic ether, in the following manner:

2 molecules of sodium were dissolved in alcohol, and, after cooling, an alcoholic solution of the hydroquinone (1 molecule) was added; thereto a little more than 2 molecules of methyl iodide were added, and the mixture heated on a water-bath, with reversed condenser, for six hours.

There is formed at first an intermediary product which crystallises from alcohol in large yellow plates. This is undoubtedly  $C_6\begin{cases}ONa\\OCH_3\\(CO_2C_2H_5)_4\end{cases}$, as it is readily converted by heating with methyl iodide into the dimethoxy-derivative. After distilling off the alcohol, water was added and the emulsion extracted with ether. The ethereal solution, after being washed with dilute sodium hydrate, left on evaporation a colorless product, which on recrystallisation from dilute alcohol was obtained in colorless needles, melting at 95°.

0.1261 gram substance dried in a vacuum gave 0.0722 gram H_2O and 0.2577 gram CO_2.

	Calculated for $C_6\left\{\begin{matrix}(OCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	56.34	55.74
H	6.10	6.36

The compound is colorless, volatile without decomposition, and easily soluble in organic solvents. The solutions show no fluorescence or coloration with ferric chloride. A chloroform solution allowed to stand for 3 days with an excess of bromine was not affected. The substance, therefore, is a benzene derivative, and not a keto-tetra-hydro-benzene derivative. This is still further confirmed by the fact that it does not undergo the slightest change when heated in a sealed tube at 100° with hydroxylamine or with phenylhydrazine.

An alcoholic solution of the substance treated with zinc dust and hydrochloric acid takes up hydrogen, just as the corresponding hydroquinone; there is formed a colorless oil, insoluble in sodium hydrate. The oil could not be made to solidify, but, treated with bromine in chloroform solution, it is converted back again to the original substance, with evolution of hydrobromic acid.

Ethyl Diacetyl-hydroquinone-tetra-carboxylate, $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.

This compound is formed by the action of acetyl chloride on the dry sodium salt. The reaction takes place instantly in the cold, with marked evolution of heat. After the acetyl chloride has evaporated, the residue is washed with dilute sodium hydrate, and then crystallised from alcohol. The acetyl compound is thus obtained in colorless plates melting at 120°.

0.1222 gram substance (dried at 100°) gave 0.0640 gram H_2O and 0.2432 gram CO_2.

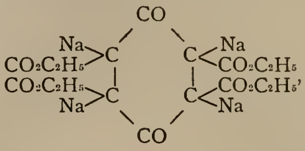
	Calculated for $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	54.76	54.28
H	5.40	5.82

The substance is colorless, volatile without decomposition, insoluble in alkalies. It is not acted upon by bromine in chloroform solution.

The solutions show no fluorescence nor coloration with ferric chloride.

Experiments to determine whether the Metal in the Salts of Ethyl p-Diketo-hexamethylene-tetra-carboxylate is bound to Oxygen or to Carbon.

In the first place, the question whether a tetra-sodium salt can be formed had to be settled. It is evident that if the sodium is bound directly to carbon, the following salt,



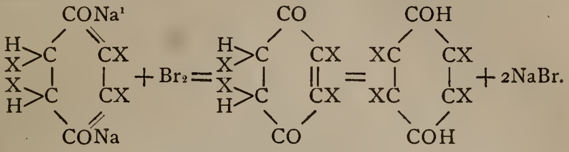
could be formed. As a matter of fact, however, such a salt does not exist. A benzene solution of the diketo compound, even when treated with a large excess of sodium ethylate, gives only a di-sodium salt. To obtain this di-sodium salt, exactly the same method was employed as in the case of the corresponding hydroquinone. It was obtained as a pale rose-colored, almost invisible, very gelatinous precipitate which it is exceedingly difficult to filter. It was therefore found advantageous to put the salt on porous clay plates and wash it with benzene. After drying at 100° and again washing with benzene, it formed, dried at 100°, a scaly, pale rose-colored product.

0.1285 gram substance gave 0.0425 gram sodium sulphate.

	Calculated for $C_6\left\{\begin{array}{l}H_2\\Na_2\\O_2\\(CO_2C_2H_5)_4.\end{array}\right.$	Found.
Na	10.36	10.71

The salt shows in every respect similar reactions to that of the corresponding hydroquinone. An aqueous solution gives pale yellow flaky precipitates with lead acetate and copper sulphate. A silver-nitrate solution is instantly reduced. Hydroxylamine hydrochloride sets free the diketo compound; acetyl chloride forms instantly a diacetyl-derivative. The alkyl iodides react, forming alcohol ethers, which have not yet been analysed. Treated with bromine water, ethyl hydroquinone-tetra-carboxylate is formed. The compound obtained thus is identical with the one obtained by reduction of the quinone, and possesses the same peculiar dimorphism.

This is a new method for converting the diketo compound, as well as ethyl succino-succinate, into ethyl hydroquinone-tetra- or para-di-carboxylate. Naturally it is not necessary to isolate the sodium salt. The reaction, it seems to me at present, can be explained as follows:



Hypothetical intermediary product, not capable of existence under ordinary circumstances (pseudo-form).

Ethyl Diacetyl-p-diketo-hexamethylene-tetracarboxylate,

$$C_6\left\{\begin{array}{l}(OH)_2\\(COCH_3)_2\\(CO_2C_2H_5)_4.\end{array}\right.$$

This substance was made in exactly the same way as the corresponding compound of the hydroquinone, except that it was not treated with sodium hydrate. Crystallised from alcohol it forms colorless needles melting at 142°.

0.1050 gram substance dried at 110° gave 0.0580 gram H_2O and 0.2080 gram CO_2.

	Calculated for $C_6\left\{\begin{array}{l}(OH)_2\\(COCH_3)_2\\(CO_2C_2H_5)_4.\end{array}\right.$	Found.
C	54.55	54.29
H	5.79	6.14

This compound possesses entirely unexpected properties. It gives a blood-red coloration with ferric chloride. It dissolves in dilute sodium hydrate and sodium carbonate solution, in the cold, much more readily than the diketo compound. The sodium salt obtained in the ordinary way with sodium ethylate and benzene, is pale rose-colored, and very much less gelatinous than the diketo salt. The salt gives reactions entirely analogous to those given by salts of phenols. Bromine water gives a product containing no bromine, and melting at about 155°, which, therefore, cannot be the diacetyl derivative of the hydroquinone. Acetyl chloride gives an acetyl derivative instantly, which has not been further studied. A silver-nitrate solution is at once reduced in the cold. These facts can only be explained on the supposition that a molecular rearrangement has taken place, like that which in all probability takes place when sodium aceto-acetic ether is treated with alkyl iodides or acetyl chloride:

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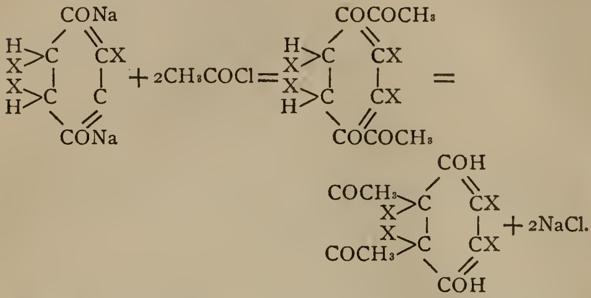
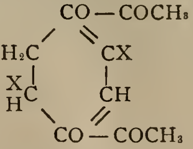
[1] One of 3 possible formulæ, as para-bonds can also be assumed. If, however, as is probable, the hydroquinone is hydrated, like the phthalic acids [Ann. Chem. (Liebig) **245**, 103], the two hydrogen atoms must be on adjacent carbon atoms.



It is noteworthy that the diacetyl derivative of ethyl succino-succinate, according to Wedel,[1] is insoluble in cold sodium hydrate. It must therefore possess the formula,  , and, if so, it must be possible to convert the substance, by means of bromine, into the diacetyl derivative of the ethyl *p*-dioxy-terephthalate.

The alcohol ethers of the diketo compound are readily formed by means of sodium ethylate and alkyl iodides. Only viscous products have as yet been obtained, and these are partly soluble and partly insoluble in sodium hydrate. Since the methylated products cannot in any way be converted into the known dimethoxy derivative of the hydroquinone, it is not improbable that a similar molecular rearrangement has taken place in this case also.

These compounds will be thoroughly investigated as soon as possible. Since the preparation of the material from durylic acid is an extremely tedious operation, the progress must be somewhat slow.

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[1] Ann. Chem. (Liebig) **219**, 86.

THE CONSTITUTION OF THE ANILIC ACIDS.

By J. U. Nef.

I.

In a previous paper[1] I have shown that nitranilic acid salts can be obtained by the action of nitrites on chloranil. The following method is now employed in the production of sodium nitranilate: 10 grams of finely pulverised chloranil are put into a flask and moistened thoroughly with alcohol. A concentrated solution of 20 grams sodium nitrite is then added, and the mixture heated; gently, at first, until the violent reaction has subsided, and finally on a water-bath for four to six hours. The residue is dissolved in hot water, and filtered from some unchanged chloranil. On cooling, sodium nitranilate separates out in great part from the filtrate. The yield is from 60–70 per cent.

Sodium nitranilate is not the sole product formed by the action of the nitrite on chloranil. There are formed sodium salts of several other acids, which are much more readily soluble in water, and therefore can easily be separated from sodium nitranilate. Especially noticeable is an apparently homogeneous sodium salt, crystallising in red needles, which, however, after repeated crystallisation gave no constant figures on analysis. Further study has proved that this substance is a mixture of salts of two, possibly three, different acids. A full treatise on these compounds, as well as on the replacement of the chlorine atoms in chloranil by various other radicals, will appear in this journal as soon as the work is completed.

As regards the sodium and potassium nitranilate from chloranil, Dr. W. Muthmann has confirmed, by comparison, the absolute physical identity with the products[2] obtained from hydroquinone. The octahedra of sodium nitranilate from pure chloranil possess a marked dichroism—reddish yellow and deep brownish red, while those from hydroquinone are pure yellow in color and possess no dichroism. The product from chloranil is rendered impure by a trace of foreign matter, which is very difficult to eliminate by repeated crystallisation.

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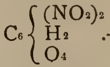
[1] Ber. d. chem. Gesell. **20**, 2027.

[2] Kindly sent to me by Dr. R. Nietzki for comparison.

By converting the salt into the free acid, however (see below), and afterwards treating with sodium hydrate, the sodium salt is also obtained in pure yellow octahedra showing no dichroism.



Nitranilic Acid, $C_6\left\{\begin{array}{l}(NO_2)_2\\ H_2\\ O_4\end{array}\right.$.—This substance (containing water of crystallisation) Nietzki[1] has already had in his hands, but on account of its instability it was not analysed. The following method was pursued in isolating the acid: 10 grams very finely pulverised sodium nitranilate (dried at 150°) were slowly added to 40 cc. concentrated nitric acid (sp. gr. 1.4, cooled to 0°). After allowing to stand for several hours, an equal volume of water was added, taking care to keep the temperature at 0° or below. The free acid separates out in yellow needles. It was filtered off, put on porous clay plates, and when dry, redissolved in a small amount of water, and separated from some unchanged sodium salt. To the filtrate one third its volume of concentrated nitric acid is added, keeping the solution at 0° or below. The acid crystallises out in needles, is filtered off, dried on clay plates, and finally allowed to stand for two days over sulphuric acid in a vacuum.

I. 0.1590 gram substance, dried at 100°, gave 0.0188 gram H_2O and 0.1804 gram CO_2.

II. 0.1945 gram substance, dried at 100°, gave 0.0252 gram H_2O and 0.2221 gram CO_2.

III. 0.1600 gram substance, dried at 100°, gave 17 cc. N_2 at 18° and 749 mm.

	Calculated for $C_6N_2O_8H_2$.	Found. I. From $C_6N_2O_8Na_2$.	II. From $C_6N_4O_{10}H_8$.
C	31.31	30.95	31.14
H	.87	1.31	1.44
N	12.17	12.30	...

Nitranilic acid is very readily soluble in water; less so in the presence of acids. Acetic ether extracts it from a dilute sulphuric acid solution, but not from an aqueous solution. The acid is soluble in organic solvents without decomposition. From acetic ether it was obtained in clear, glistening yellow prisms. An aqueous solution of the acid decomposes very quickly on warming, with liberation of prussic acid, and formation of an organic acid giving a yellow barium salt. The same reaction takes place, only more slowly, in the cold. The pure dry substance, however, can be kept for months without undergoing the slightest decomposition. On heating, it explodes without melting at a high temperature.

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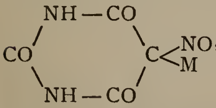
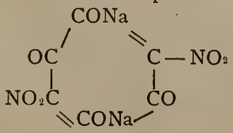
[1] Ann. Chem. (Liebig) **215**, 139.

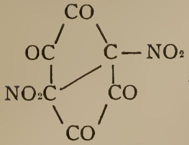
The acid decomposes chlorides, sulphates, and nitrates, forming nitranilates and free hydrochloric, sulphuric, or nitric acid.

Treated with hydroxylamine hydrochloride, an oxyammonium salt separates out directly: $C_6N_2O_8H_2+2NH_4OCl=C_6N_4O_{10}H_8+2HCl$.

Chemical Conduct of Nitranilates.

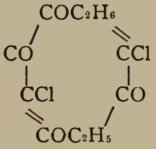
The salts of nitranilic acid possess at ordinary temperature an extraordinary stability. They are all explosive, especially the mercuric salt. In their entire chemical and physical behavior they show a great resemblance to the salts of the nitro-derivatives of the fatty series, which undoubtedly have the metal bound directly to carbon. They also show resemblance to the salts of fulminic, barbituric, and dilituric acids. The salts of dilituric acid,  especially, are very stable, and many of them are not decomposed by mineral acids. Finally, the nitranilates show in their chemical behavior a marked difference from that shown by salts of phenols (see preceding paper). Hydroxylamine hydrochloride does not set free the acid, but forms a stable oxyammonium salt. The silver salt is very stable, and can be heated in a sealed tube at 130° for 6–8 hours with methyl iodide without change. By treating the sodium salt with bromine water, it was not found possible under any conditions to obtain a product free from bromine, but the bromine replaced the sodium atom directly.

If sodium nitranilate possesses the commonly accepted constitution,  , it is difficult to see why, by the action of one molecule bromine, a compound of the formula,



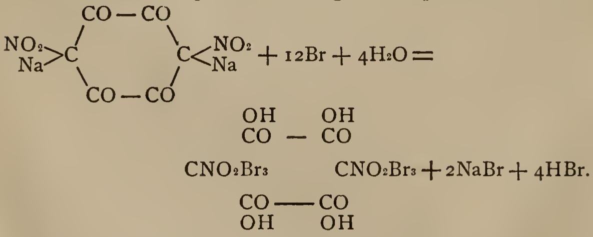
, cannot be formed. Such a reaction would be entirely analogous to that noticed by myself in the case of the sodium salts of ethyl *p*-diketo-hexamethylene-tetracarboxylate and of ethyl succino-succinate (*vid.* preceding paper). The presence of negative groups cannot be the cause of the different chemical behavior, since the sodium salt of tetrachlor-hydroquinone is an unstable compound, and gives reactions entirely analogous to those given by other phenol salts.

Although it was not possible, under any conditions, to obtain alcohol ethers or an acetyl derivative of nitranilic acid, Stenhouse[1] has obtained the ethyl ether of chloranilic acid. This compound, if it has the formula



, must take up bromine, which as a matter of fact it does not.

On treating sodium nitranilate with 12 molecules bromine, the closed chain of six carbon atoms is quantitatively split up into oxalic acid and brompicrin, according to the equation,



This, to my knowledge, is the first observed quantitative splitting up of a closed chain of six carbon atoms into fatty compounds.

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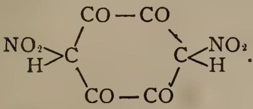
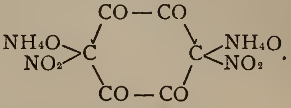
[1] J. Chem. Soc. (London), **23**, 4.

The above mentioned facts seem to me to make the following constitution of nitranilic acid probable,



It is therefore nothing but a para-dinitro-derivative of tetra-keto-hexamethylene.

Oxyammonium-nitranilate,



This substance is formed on adding hydroxylamine hydrochloride to a solution of nitranilic acid, or of sodium nitranilate (hot). In the former case it separates out as a yellow granular powder; in the latter, in long dark-yellow plates. Crystallised once from hot water it is pure.

I. 0.2130 gram substance, dried at 110° and mixed with lead chromate, gave 0.0568 gram H_2O and 0.1900 gram CO_2.

II. 0.1452 gram substance, dried at 110°, gave 0.0422 gram H_2O and 0.1287 gram CO_2.

III. 0.2080 gram substance, dried at 110°, gave 34.5 cc. N_2 at 17.5° and 757.5 mm.

	Calculated for $C_6N_4O_{10}H_8$.	Found. I. From $C_6N_2O_8Na_2$.	II. From $C_6N_2O_8H_2$.
C	24.33	24.52	24.18
H	2.69	2.96	3.23
N	18.92	19.42	...

On being heated, the substance explodes at a high temperature without melting. Obtained from sodium nitranilate, it possesses a dark-yellow color; from nitranilic acid, however, a pure yellow color. The form of the crystals is the same in both cases. The above-mentioned impurity in the case of the sodium salt, therefore, goes over into the oxyammonium salt. When added to cold concentrated nitric acid (1.4), the salt is converted into nitranilic acid (analysis above).

Noteworthy is the action of the oxyammonium salt with hydroxylamine hydrochloride. On boiling 10 grams of the salt, suspended in water, with an excess of hydroxylamine hydrochloride

(4 molecules), a violent evolution of gas (nitrogen, carbon dioxide, and some prussic acid) is noticed after a while. When the gas has ceased to come off, about 2 grams of substance crystallise out from the yellow solution on cooling, in long yellow needles. A series of analyses have proved that this compound contains the group C_6N_5 or C_5N_4. It loses one atom of nitrogen when treated with concentrated nitric acid, and is converted into a substance containing the group C_6N_4 or C_5N_3. The products obtained explode on heating; it would be premature to attempt to give them formulæ, since, in all probability, they contain water of crystallisation.

Action of Bromine on Sodium Nitranilate.

On adding a little more than the calculated amount of bromine (105 grams) to 30 grams very finely pulverised sodium nitranilate suspended in water (250 cc.) cooled to 0°, the color of the bromine rapidly disappears, with marked evolution of heat; at the same time a vapor with a powerful odor, and strongly affecting the eyes, is noticed. Finally, there is found at the bottom of the vessel a heavy oil colored yellow by bromine. After standing for half an hour, the excess of bromine is got rid of by sulphurous acid, and the oil extracted with ether. The ether is then distilled off, and the residual oil, after being heated for some time at 100°, is distilled over with steam. By means of a drop-funnel it is separated from water, and then dried with fused calcium chloride.[1] The analysis of the oil gave figures agreeing with brompicrin, with which it also coincides in all its properties.

0.4654 gram substance gave 0.0109 gram H_2O and 0.0689 gram CO_2.

0.4944 gram substance gave 23 cc. N_2 at 30° and 750 mm.

0.2537 gram substance gave, heated with CaO, 0.480 gram AgBr.

	Calculated for $C\begin{cases}Br_3\\NO_2\end{cases}$.	Found.
C	4.04	4.04
Br	80.52	80.50
N	4.72	5.17
H	...	.26

In the aqueous solution is found on evaporation, besides hydrobromic acid, nothing but oxalic acid and sodium bromide. The oxalic acid was obtained in long transparent prisms melting in their water of crystallisation at 101.5°. On standing over sulphuric acid it lost its water of crystallisation, and crumbled to a white powder, melting, with decomposition, towards 188°. An analysis of the calcium salt, dried at 110°, gave the following figures:

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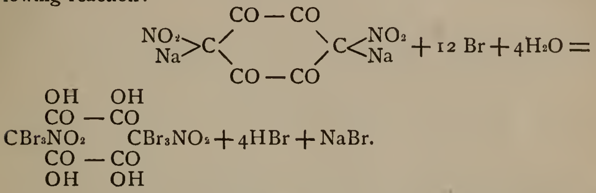
[1] Victor Meyer, Ann. Chem. (Liebig) **180**, 122.

0.2374 gram substance gave 0.2188 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.4	27.11

Sodium nitranilate is therefore split up by means of bromine into brompicrin, $C{<}^{Br_3}_{NO_2}$, and oxalic acid, according to the following reaction:



A quantitative determination with 3 grams sodium nitranilate (dried at 150°) gave:

3.190 grams calcium oxalate, $CaC_2O_4.H_2O$, dried at 110°. 3.197 grams, calculated.

30 grams sodium nitranilate gave 66 grams crude $C{<}^{Br_3}_{NO_2}$, calculated 65.3 grams.

It now seemed probable that the salts of the other anilic acids could be split up in an analogous[1] manner with bromine. Experiments begun with potassium chloranilate have indeed confirmed this opinion. On treating the substance with bromine, exactly as above, I obtained a heavy colorless oil readily volatile with steam, and having an odor very much like that of chloroform. It is very probable that this substance is tribrom-chlor-methane, CBr_3Cl.[2] Besides this oil, oxalic acid is formed, but in much smaller quantity than in the case of sodium nitranilate.

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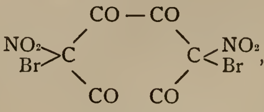
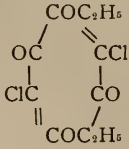
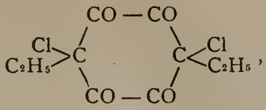
[1] The sodium salt of the so-called ethyl-quinone-dioxy-dicarboxylate can, in all probability, be split up into tribromacetic ether and oxalic acid. The free ester gives with chlorine, as is well known, ethyl tetra-chlordiketo-adipinate. Hantzsch and Zeckendorf, Ber. d. chem. Ges. **20**, 1309.

[2] Besides the oil, I obtained traces of a substance crystallising in colorless plates (mpt. 88°) which correspond with CBr_4 in properties.

Attention is called to the fact that the free anilic acids, on treatment with halogens, yield totally different products. Thus bromanilic acid gives with bromine, per-brom-acetone.[1] Chloranilic acid gives with bromine the symmetrical tetra-brom-dichloracetone;[2] with chlorate of potash and hydrochloric acid, tetrachlorinated acetone and diacetyl.[3]

A number of experiments were made with the idea of obtaining from sodium nitranilate with bromine an intermediary product, such as , but without success. On treating the nitranilate with but one molecule bromine, brompicrin is formed. On the other hand, the experiments just begun with potassium chloranilate promise a better result.

Finally, attempts to obtain a methyl ether or an acetyl derivative of nitranilic acid were fruitless. While acetyl chloride is without action on the sodium salt at ordinary temperature, there is formed, on heating in a sealed tube at 100°, chloride of sodium with total decomposition of the nitranilic acid molecule. Methyl iodide does not act on the silver salt even when heated for 6–8 hours in a sealed tube at 130°. On heating at 180°–200°, decomposition takes place with the formation of silver iodide, and a silver salt of an organic acid containing iodine.

On the other hand, Stenhouse[4] has shown that silver-chloranilate, when heated with ethyl iodide, gives an ethyl ether melting at 107°. This substance, which is volatile without decomposition, is extremely stable in the presence of bromine or nitric acid. A chloroform solution of the substance, allowed to stand a long time with an excess of bromine, is not changed. A compound having the formula  must necessarily take up bromine, while a compound, , could not be affected by bromine.

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[1] Hantzsch and Schniter; Ber. d. chem. Ges. **20**, 2040.

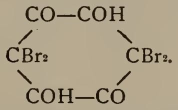
[2] Levy and Jedlicka; Ibid. **20**, 2319.

[3] Levy and Jedlicka; Ibid. **21**, 318.

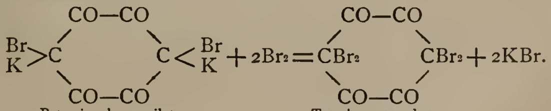
[4] Journ. Lond. R. Soc. Proc. **23**, 4.

The experiments with ethyl chloranilate, and with the salts of chloranilic and nitranilic acid, will be continued. It seems to me that the above facts already make it probable that the anilic acids are para-derivatives of tetra-keto-hexamethylene.

POSTSCRIPT.

A paper by Hantzsch in the Berichte der deutschen chemischen Gesellschaft, Vol. 21, p. 2421, has just been received. By the action of two molecules of bromine in water on potassium bromanilate, Hantzsch has obtained a colorless product to which he has given the formula, 

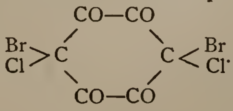
From the results presented in the foregoing paper, it will be evident that the compound cannot possess this formula. The reaction simply takes place as follows:



Potassium bromanilate.

Tetrabrom-tetraketo-hexamethylene.

The so-called bromanilic acid dibrom addition-product is therefore nothing but tetrabrom-tetraketo-hexamethylene.

By the action of two molecules of bromine on potassium chloranilate, I have also obtained a colorless product soluble in ether, which is probably  These facts, as well as the further results presented in Hantzsch's paper, do but confirm the constitution of the anilic acids as being para-derivatives of tetraketo-hexamethylene.

The action of bromine on salts having the metal bound directly to a carbon atom is different in that the bromine takes the place occupied by the metal, *i. e.* substitution takes place. In the other case, where the metal is bound to carbon by means of oxygen, products free from bromine are obtained (see the two foregoing papers).

LA FAYETTE, IND., *Sept.* 30, 1888.

SEPARATION OF ALUMINIUM AND ZIRCONIUM.

BY I. THOMAS DAVIS, JR.

While studying some of the iodine compounds of zirconium it was found that the iodate, when precipitated from neutral or very feebly acid solutions, gave filtrates in which no zirconium could be detected with ammonia. This apparent insolubility and the fact that aluminium iodate, according to Berzelius,[1] was deliquescent, suggested the possibility of separating these metals by means of an alkaline iodate. Solutions of aluminium refused to show the least signs of precipitation when treated in a manner similar to that by which complete precipitation had been obtained from zirconium salts. In order to examine the method quantitatively, a solution of zirconium chloride in hydrochloric acid was employed. This solution was prepared as follows:

Zircon was decomposed with sodium carbonate and hydrate, the fusion boiled out repeatedly with water, and the residual sodium zirconate decomposed with sulphuric acid. This solution was evaporated carefully to dryness, and kept at a heat just below redness for half an hour. It was then dissolved in water to which a little sulphuric acid had been added, and precipitated with ammonia. The resulting hydrate was dissolved in hydrochloric acid, and the zirconium precipitated several times with sodium thiosulphate, to separate the last trace of iron. The zirconium was finally precipitated with ammonia, washed until the filtrate no longer reacted for chlorine, dissolved in hydrochloric acid, which was added in sufficient quantity to prevent the deposition of an oxychloride, and diluted to the proper strength. It contained in round numbers 5 per cent. of hydrochloric acid by weight.

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[1] Lehrb. ed. 1843-48; **3**, 479.

In order to standardise this solution, the zirconium was precipitated with ammonia, using to a certain extent the same precautions which are to be observed when aluminium is precipitated in a similar manner, and Nos. (1) and (2) represent duplicate determinations.

	Weight of Solution.	ZrO_2 found.	ZrO_2 in 25 grams.
(1)	25.344 grams	.1696 gram	.1673 gram
(2)	25.322	.1686	.1669

The average, .1671 gram, has been taken as representing the correct amount of the tetrachloride, $ZrCl_4$, in terms of the dioxide, ZrO_2, in 25 grams of the solution.

Qualitative experiments seemed to point to the possibility of complete precipitation, as an oxyiodate, when the solution contained a moderate amount of free acid.

	Weight of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(3)	25.325	.1693	.1604	.0089 —
(4)	25.297	.1691	.1576	.0115 —

In (3) and (4) the acid was neutralised with sodium carbonate, and hydrochloric acid added in such quantity that the solutions contained 1 per cent. by weight. Sodium iodate was then added in excess and the solutions brought to a boil, and fifteen minutes afterwards filtered, washed with hot water until the filtrate and washings in each case amounted to about 400 cc. They were dried and ignited together with the filters. During the ignition slight explosions took place, and once the lid of the crucible, which contained (4), was thrown off. At the same time it took prolonged ignition at the highest heat of the blast-lamp to arrive at constant weight, small quantities of iodine vapors being evolved. These vapors were due to sodium iodate retained by the precipitate, as the zirconium salt seems to part with its iodine at a heat below redness. Hence, the idea of igniting this iodate or of precipitating zirconium from solutions containing much acid was abandoned.

Wts. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(5) 20.300	.1357	.1380	.0023+
(6) 20.159	.1347	.1349	.0002+

In (5) and (6) the acid of the zirconium solution was neutralised with sodium carbonate, which was added until a permanent precipitate was formed. This was dissolved in the smallest possible quantity of dilute hydrochloric acid, sodium iodate added in excess, and the solutions boiled for 15 minutes. Instead of filtering immediately, as in (3) and (4), it was thought safest to allow them to stand some time. They were, therefore, allowed to stand over night, then filtered, washed with hot water, dissolved in hydrochloric acid, of which it took a considerable amount, even while hot, precipitated with ammonia, ignited, and weighed. Unfortunately in (5) the washing was very imperfect, but in (6) and all subsequent experiments the washing was continued until the filtrates no longer gave a reaction for chlorine.

Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(7) 10.086	.0674	.0674	0
(8) 10.088	.0674	.0682	.0008+
(9) 20.263	.1354	.1352	.0002—
(10) 20.408	.1364	.1365	.0001+

(7), (8), (9), and (10) were carried on exactly like (5) and (6), with the exception that to (9) 5 grams of sodium chloride were added, and to (10) 10 grams. Precipitation seems to be complete, and sodium chloride is without action on the iodate. In filtering the iodate, which is flocculent, it is safest to use Swedish paper, as the precipitate can be more readily washed off without loss than from some of the other papers used.

These experiments having turned out so satisfactorily, it was thought possible that complete precipitation might take place in solutions containing some free acid, but not nearly in such quantity as had been employed in (3) and (4). To determine this point, (11) and (12) were made.

Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(11) 30.337	.2028	.1996	.0032—
(12) 30.410	.2032	.2010	.0022—

The acid was neutralised as before, and enough hydrochloric acid added to make the solution contain about 0.1 per cent. of it.

Aluminium chloride was also added in quantity about three times that of the zirconium chloride present. The solution of aluminium chloride was prepared by precipitating pure potassium alum several times to separate all sulphuric acid, and the hydrate dissolved in hydrochloric acid. Its strength was only approximately known. It is evident that precipitation, even in the presence of this small amount of acid, is incomplete. However, no aluminium seems to have been thrown down. The solutions, then, previous to precipitation must be nearly neutral. Therefore, in (13–14) and (15–16) the precipitation was carried on as in (5) and (6).

Wt. of Solution.	ZrO_2 used.	ZrO_2 found.	Error.
(13) 10.097	.0675	.0673	.0002—
(14) 10.070	.0673	.0671	.0002—
(15) 49.490	.3308	.3302	.0006—
(16) 49.398	.3302	.3301	.0001—

In (13) and (14) the quantity of aluminium was about three times that of the zirconium, while in (15) and (16) equal quantities were used. These numbers seem to be within the error of analysis. Therefore, to separate these two metals, I proceed as follows: Their solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is dissolved in the smallest possible quantity of dilute hydrochloric acid, and sodium iodate added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand 12 hours, filtered, washed down with boiling water, dissolved in hydrochloric acid, and finally precipitated with ammonia, ignited, and weighed. A convenient strength of solution is 100 mgs. ZrO_2 in 100 cc.

Three analyses of the zirconium salt proved it to be an oxyiodate of variable composition. Several attempts were made to separate iron, both in the ferrous and ferric state, but without success. This metal must be removed from the mixture of aluminium and zirconium previous to their treatment with sodium iodate.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XVII.

Communicated by F. P. DUNNINGTON.

143.—EXAMINATION OF A COPPER SLAG OF RED COLOR CONTAINING ARTIFICIAL CUPRITE.

BY J. L. JARMAN AND J. F. McCALEB.

On a former occasion a specimen of similar slag was examined in this laboratory,[1] when attention was drawn to the pale yellow powder remaining on digestion in aqua regia.

The specimen in hand has been received from the Canton Copper Works of Baltimore, Md., and has been more fully examined, with the following results. It is very hard and tenacious, breaks with conchoidal fracture and knife-like splintery edges, having scattered throughout its mass small spherical cavities and also very minute beads of metallic copper ; is opaque, with a dark scarlet color. Sp. grav. = 3.486. H. = 4.8. Analysis of the entire slag affords:

SiO_2	38.039
Cu_2O	47.489
Al_2O_3	2.001
FeO	2.829
CaO	2.525
MgO	.404
K_2O	.549
Na_2O	5.920
	99.756

A thin section of the slag was examined under the microscope and found to consist of a transparent matrix of pale yellow color, in which is closely imbedded minute transparent crystals of cochineal red color, mostly in cubical and rectangular forms, similar to those of common salt, with less distinctly shown octahedra. All of these crystals have a thickness of about .002 millimeter. A portion of the slag was brought to an exceedingly fine powder and digested upon a water-bath with 8 per cent. nitric acid, which removed 46.29 per cent. of its mass, and of this 43.49 per cent. was cuprous oxide. The resulting pale yellow powder showing no red fragments under the microscope, was then digested for two hours in 20 per cent. sodium hydrate, which was found to dissolve but .5 per cent. of silica. From these results we infer that the red color of such slag is due only to cuprous oxide and not to any cuprous silicate; and we note that this cuprous oxide is in the form of native cuprite, similar also to that recently observed by Professor W. G. Brown.[1]

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[1] This Journal 8, 429.

The pale yellow powder thus prepared, and insoluble both in aqua regia and in sodium hydrate, was further examined with the following results: sp. gr. = 2.31; H. = 4.8; fusible at 2 without change of color, but in the oxidising flame, and more readily when also in a borax bead, it affords a blue glass The analysis gave:

SiO_2	69.22	1000
Al_2O_3	4.84	61
FeO	5.74	70
CaO	3.33	
MgO	.89	
Cu_2O	5.65	92
K_2O	.61	
Na_2O	10.34	
	100.62	

This oxygen ratio suggests petalite, in which the ratio is $\dot{R} : \dddot{R} : Si = 1 : 4 : 20$; but in this slag we have $\dot{R} : \dddot{R} : Si = 8 : 3 : 50$.

The highly acid nature of this slag is the more remarkable when we recollect that the basic cuprous oxide was distributed throughout the mass, and had, no doubt, separated in crystals from the mass when in a state of fusion.

144.—A COMPARISON OF THE RATES OF SOLUTION OF GYPSUM AND ANHYDRITE.

By J. F. McCaleb.

Both gypsum and anhydrite are employed as fertilisers, but since the former contains 20 per cent. of water, while the latter contains none, it is of economic interest to ascertain whether or not each is to be valued in proportion to the amount of calcium sulphate in it. Both of these bodies are rather insoluble in water, and are employed under conditions which call for solution before any effect is produced.

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[1] Am. J. Sci. **32**, 379.

It was therefore first undertaken to determine the rates of solution by digestion of the powdered substances, but it was soon observed that the flexible crystals of selenite could not with certainty be brought to the same state of subdivision as the harder and more brittle anhydrite, and the rate of solution depended too largely upon the degree of fineness. The experiment was then conducted as follows: A compact lump of each of the several specimens was cut to present some flat surface, and partially covered with paraffin, leaving exposed from 6 to 9 sq. cm. area. Each of these was suspended by a platinum wire, just beneath the surface of four liters of distilled water contained in a tall specie jar. These were allowed to stand undisturbed at a temperature varying from 19° to 23° C. At the end of a week the lumps were temporarily removed, the contents of each jar mixed, and a sample of 100 cc. taken, in which the SO_3 was determined as $BaSO_4$, and from this the $CaSO_4$ was calculated. No specimen of crystallised anhydrite was available. The following specimens were used:

A. Gypsum "pure," pink micaceous mass, Saltville, Va.
B. Gypsum "pure," white massive, Nova Scotia.
C. Selenite "pure," honey-yellow crystal, Montmartre.
D. Anhydrite "impure," grey massive, Salzberg.
E. Anhydrite "pure" (97 per cent.), greyish massive, Nova Scotia.
F. Gypsum and anhydrite mixed, white massive, Nova Scotia.

Amounts of calcium sulphate in grams dissolved from each square centimeter of surface in one week:

A.	B.	C.	D.	E.	F.
.2388	.2219	.1177	.0666	.0601	.2184

The different results from the three hydrated specimens A, B, and C are explained by their respective forms, A being composed of an aggregation of small crystals, which greatly increased the actual surface exposed to the solvent. In B the crystals are minute and more compacted. With C, only a single crystal face (clino-diagonal) was exposed, which was uniformly removed by the solvent.

As to the specimens of anhydrite D and E, D contained of anhydrite about 81 per cent., selenite about 13 per cent., sand and organic matter about 6 per cent.; E contained of anhydrite about 97 per cent.; and we note that the greater solubility of the selenite present in D has given more to the solution than 19 per cent. of anhydrite would have done.

Specimen F, being composed partly of anhydrite and of gypsum, was dissolved irregularly, leaving a rough surface with seams and pits, and clearly showing the varying composition of the surface exposed.

We can best judge of the relative rate of solution of gypsum and anhydrite by comparing the results of B and E, since these were very similar in structure and appearance. From these we infer that, where in powder of the same degree of fineness and in contact with a large amount of water, the anhydrite requires for its solution from three to four-fold the time that the gypsum does.

Continuing these observations, to ascertain something of the action of the solvent as it becomes more nearly saturated, specimens B, C, and D were exposed for a longer time, and afforded the following:

Amounts of calcium sulphate in grams dissolved for each sq. centimeter of surface.

	1 week.	2 weeks.	3 weeks.	4 weeks.	5 weeks.
B	.2219	.4638	.6788	.8168	.8768
C	.1177	.2021	.3250	.4179	.4893
D	.0666	.0999	.1514	.1881	.2398

From the foregoing we note that the ratio between the amounts dissolved from the several specimens during each of the weeks continues about the same. The rate of solution diminished a little as the solvent became more nearly saturated, while the smaller amounts dissolved from all three specimens in the 2d and 4th weeks was probably due to a change of temperature, of which no record was kept. The largest amount dissolved was 5.87 grams from B in five weeks, and equivalent to about 75 per cent. of saturation.

145.—ON THE HYDRATION OF CALCIUM SULPHATE.

By J. F. McCaleb.

In close relation to the preceding article is the problem, At what rate is anhydrous calcium sulphate converted into the hydrate?

Ordinary "Plaster of Paris" will in a few minutes combine with water with which it is mixed; on the other hand, extensive beds of anhydrite are found which have been by long exposure altered, in part, to gypsum. The question then arises: At what rate will this hydration take place with native anhydrite and with different forms of dehydrated gypsum when kept in contact with water?

It was first ascertained that, at common temperature, and over sulphuric acid, all water is taken up from admixture with either hydrated or anhydrous calcium sulphate, while none is removed from chemical combination.

The specimens of anhydrite designated in the preceding article as D and E were employed, and also a specimen, G, obtained by bringing selenite, C, to a bright red heat. One gram of each specimen in fine powder was weighed into a watch-glass, moistened, and kept over water under a bell-jar. From time to time it was found necessary to renew the addition of water to the watch-glass. In order to ascertain the extent of hydration, the watch-glass, with contents, was dried over sulphuric acid and weighed. As the hydrate was formed there was some caking of the powder, which interfered with the regularity of the change which was taking place.

Several watch-glasses, each containing one gram of anhydrite D, were similarly exposed to moisture at temperature 20° to 25° C., and absorbed of water as follows:

Weeks exposed:	4	8	12	16	20	28	36
Water absorbed:	.0308	.0488	.0629	.0700	.0803	.0873	.0949

From which we note that, upon mere digestion with water, where the solution is not removed, the rate of combination is a slow one, gradually diminishing, and under the conditions given would probably be completed in two years.

One gram of each of the three specimens D, E, and G was kept moist at 25° to 30° C. and found to combine with water, as follows:

	1 week.	2 weeks.	3 weeks.
D	.0209	.0357	.0493
E	.0072	.0155	.0234
G	.0022	.0048	.0073

From this it appears that the rate at which the hydration takes place varies greatly with the different specimens, and probably this rate is determined by the extent to which these different specimens have been compacted by the heat which effected their dehydration; for specimen D still retained a small amount of water, and specimen G had been exposed to a bright red heat. To gain some information on the latter point the following investigation was made:

146.—ON THE SPECIFIC GRAVITY OF CALCIUM SULPHATE.

By J. F. McCaleb.

In making these estimations a specific gravity bottle was used, and in order to avoid any hydration of the substances, a paraffin oil having a high boiling point was employed. As this oil expands greatly on being heated, it was found necessary to pay special attention to all changes of temperature and make due corrections.

Most of the following figures are averages of concording results, and all are given with reference to water at 15° C.

1. "Plaster of Paris" obtained by heating crystallised selenite (C) to 200° C., sp. gr. = 2.577.
2. Same selenite heated to dull red, sp. gr. = 2.911.
3. Same selenite heated to bright red, sp. gr. = 2.890.
4. Same selenite heated on platinum, just melted before hot blast blowpipe, sp. gr. = 2.796.
5. Same selenite, in a clay crucible and well luted, was packed within one of graphite and heated in a wind furnace, using gas carbon for fuel. The resulting glassy mass showed numerous minute cavities (no doubt due to escaping gas when in fusion); it gave sp. gr. = 2.654.
6. Anhydrite (E, 97 per cent. pure) massive, sp. gr. = 2.907.

I append from the tables of Professor Clark:[1]

Selenite, sp. gr. = 2.30 to 2.33.
Anhydrite, sp. gr. = 2.92 to 2.98.
$2CaSO_4 + H_2O$, sp. gr. = 2.757.

Comparing the results of experiments 1, 2, and 6, we note that after the water has been expelled, up to a certain point, further heating compacts the aggregation of the molecules of the calcium sulphate until it attains the specific gravity of anhydrite, and in this condition, whether produced in nature or artificially, combination with water takes place very slowly.

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[1] Constants of Nature, Part I, pp. 81, 82.

We note also from 2, 3, 4, and 5 that as the heating is carried beyond a dull red, the specific gravity is diminished; possibly the explanation of this is found in the small cavities seen in 5, which may have been present but microscopic in specimens 3 and 4.

The peculiar hydrate, $2CaSO_4 + H_2O$, mentioned above, was formed within a steam boiler,[1] and probably at a temperature of 150° C. If we imagine this substance to be deprived of its water, without changing the aggregation of the remaining molecules—that is, not altering its volume—its specific gravity would then be $2.757 \times \frac{290 - 18}{290} = 2.585$. This latter figure is practically identical with the specific gravity of plaster of Paris (2.577) as stated above.

Since it has recently been shown by Messrs. Shenstone and Cundall[2] that gypsum may be dehydrated in dry air at 100° C., and even at 70° C., it would be of interest to ascertain what is the specific gravity of the anhydrous calcium sulphates thus produced, and how they compare with the hydrates of calcium sulphate which have been formed under pressure at different temperatures.

147.—ANALYSIS OF OYSTER SHELLS AND OYSTER SHELL LIME.

BY L. P. BROWN AND J. S. H. KOINER.

The sample of shell, retaining the usual small amount of mud, was taken from the dump at a lime-kiln near Baltimore, where the burning of the shell is effected in the following manner. It is fed into a conical brick-lined shaft, together with one-tenth of its bulk of dust of either anthracite or bituminous coal, which latter suffices to maintain the combustion. The specimen of lime was taken immediately from the grate of the kiln, and, of course, contains the ash of the coal dust.

Analysis afforded the following; the result for shell being the average of two independent analyses.

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[1] Johnston, P. M. (2), **13**, 325.

[2] Jour. Chem. Soc. **307**, 544.

	Oyster Shell.	Shell-Lime.
CaO,	52.14	85.49
CO_2,	41.61	.70
MgO,	.25	.31
FeO,	.17	...
Fe_2O_3,	...	.33
Al_2O_3,	.08	.42
Na_2O,	.32	.69
K_2O,	.03	.11
SO_3,	.16	.66
P_2O_5,	.04	.15
Cl,	trace	trace
SiO_2 soluble,	.06	1.14
Insoluble residue,	3.24	5.15
Organic matter,	2.32	...
Nitrogen,	.14	...
Water,	...	3.97
	100.42	99.12

From the former we note, that by present prices the shell contains per ton not more than 50 cents worth of ammonia, which is lost in the burning. This small amount of nitrogen would not warrant the use of any mechanical means of subdivision of the shell, as has been proposed and practised on a small scale. From the latter analysis we see that shell lime compares favorably in purity with the fair grades of stone lime.

148.—ANALYSIS OF "TOBACCO SCREENINGS" REJECTED IN THE MANUFACTURE OF TOBACCO.

By L. P. Brown.

This material consists of the small fragments of stems and leaves which with the dust are sifted from tobacco after it has been ground, in the process of preparing smoking tobacco.

Much of this substance is mixed in certain manufactured fertilisers, and is not unfrequently applied directly as a top-dressing to grass, etc.

The sample examined was taken from a lot of the screenings shipped from Lynchburg, and afforded the following:

Water lost at 100° C.,	10.27
Total (crude) ash,	43.40
Organic matter (by difference),	46.33
	100.

In the Organic Matter.

Nicotine,	.36	
Albumenoids and nitrates,	6.96	
(Total nitrogen) equivalent to ammonia,		1.48

Constituents of the ash:

	In 100 parts of Screenings.	In 100 parts of Ash.
K_2O,	1.187	2.89
Na_2O,	.506	1.23
CaO,	2.796	6.81
MgO,	.346	.84
Al_2O_3,	.192	.47
Fe_2O_3,	.212	.52
SiO_2,	33.760	82.32
P_2O_5,	.296	.72
SO_3,	.483	1.14
Cl,	.451	1.10
SiO_2, soluble,	.907	2.21
Deduct O, equiv. to Cl,	...	.25
	41.136	100.00

In estimating the value of this substance as a fertiliser, we must consider the nicotine, which acts as an insecticide, in addition to the organic matter and the plant food ingredients. As to the latter and the nitrogen, there is contained in 2000 pounds, reckoning at present commercial prices, potash, phosphoric acid, and nitrogen to the value of $6.

149.—ANALYSIS OF A "FIRE EXTINGUISHER."

By R. A. Baird.

From the published analyses of a number of these fire-extinguishing liquids it appears that they are composed essentially of an aqueous solution of one or more of the following bodies: sodium, potassium, ammonium, magnesium, and calcium chlorides and sulphates, and occasionally borax and sodium acetate.

In the examination of a new brand of these articles I found it was composed largely of sodium hyposulphite. As I am not aware that this substance has been mentioned heretofore as being used for this purpose, an analysis of it has been made by Mr. Baird, with the following results: The vessel contained about 5 gills, 600 cc. of solution, in which there were found:

Sodium hyposulphite, . . .	255.55	grams.
Sodium chloride, . . .	48.12	"
Ammonium chloride, . . .	12.60	"
Ammonia, free, . . .	12.24	"
	328.51	

150.—ANALYSIS OF PYROLUSITE FROM CRIMORA MINE, AUGUSTA CO., VA.

By J. L. Jarman.

The ores obtained from this mine have maintained for some years a reputation for peculiar purity, samples from large cargoes showing 79 to 82 per cent. of manganese oxides and over 57 per cent. of metallic manganese. The larger portion of this ore consists of psilomelane mixed with about one-third as much pyrolusite, occurring in nodular masses and distributed through a disintegrated calcareous shale. I have recently received a fine mass of this ore, weighing about fifty pounds, and from it obtained material for the following analysis by Mr. Jarman. It consists of a network of fibrous crystals, closely matted; color, grey; streak, black; H. = 2.7; sp. gr. = 4.69; infusible. Analysis gave:

		Molec. ratio.
MnO, ...	78.270	110.24
O, ...	17.610	110.06
Fe_2O_3, ...	.617	.38
CaO, ...	.094	.18
NiO, ...	.225	.30
CoO, ...	.269	.36
K_2O, ...	.179	.18
Na_2O, ...	.232	.37
H_2O, ...	2.085	1.63
Insol. res., . . .	.293	
	99.874	

Omitting the moisture, this shows the mineral to contain 98 per cent. of MnO_2.

It appears of interest to record this occurrence of pyrolusite of unusual purity from an American locality.

UNIVERSITY OF VIRGINIA, *Sept.*, 1888.

ON THE RELATIVE STABILITY OF THE ALKYL BROMIDES.[1]

BY FELIX LENGFELD.

A short time ago, a careful study of the methods which seemed most likely to lead to satisfactory results in the investigation of the relative stability of the alkyl bromides, was made by Remsen and Hillyer,[2] and it was shown that of all the reactions studied, those with salts of silver and caustic soda were most promising. At the suggestion of Professor Remsen, I have investigated somewhat in detail the decomposition of a number of the alkyl bromides under the influence of sodium and potassium hydroxides, ammonia, silver nitrate, nitric acid, sulphuric acid, and a mixture of silver nitrate and nitric acid, and the results are recorded in this paper.

Substances Used.

As the alkyl bromides used are insoluble in water, the reagents were used in alcoholic solution. They were made as follows:

The solutions of sodic hydrate were made by dissolving sodium in 99.5 per cent. alcohol, and were $\frac{n}{5}, \frac{n}{10}, \frac{n}{20}, \frac{n}{40}$ and $\frac{n}{50}$. They were standardised each time before using.

The solution of potassic hydrate was made in a similar way and was $\frac{n}{10}$.

The solution of ammonia was $\frac{n}{10}$, and was made by dissolving ammonia in 99.5 per cent. alcohol.

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[1] From the Author's Dissertation for the Degree of Doctor of Philosophy at the Johns Hopkins University, 1888.

[2] This Journal **8**, 251.

The solution of silver nitrate, made by dissolving the salt in 85 per cent. alcohol, was $\frac{n}{10}$.

The solution of silver nitrate and nitric acid was made by adding to the silver nitrate solution just described, nitric acid in the proportion of 6.3 grams to the liter.

The solutions of nitric and of sulphuric acids were made by dissolving the acids in 85 per cent. alcohol and were $\frac{n}{10}$.

The bromides used were ethyl bromide, boiling at 38°–39°; propyl bromide, boiling at 70°–71.5°; butyl bromide, boiling at 99°–101°; isopropyl bromide, boiling at 60°–63°; isobutyl bromide, boiling at 92°–93°; isoamyl bromide, boiling at 119°–120°; tertiary butyl bromide, boiling at 71°–73°, and ethylene bromide, boiling at 131.5°–132°. The propyl, isopropyl, isobutyl and isoamyl bromides were prepared from Kahlbaum's by washing with water, drying over calcic chloride, and subjecting to fractional distillation. The ethyl bromide was made by the action of bromine and phosphorus on alcohol, and the ethylene bromide by the action of bromine on ethylene. The butyl bromide was prepared from butyl alcohol made by Lieben and Rossi's method.[1] Instead, however, of making the bromide, as was done by these chemists,[2] by heating the alcohol and hydrobromic acid in a sealed tube, I made it by the action of bromine and red phosphorus on the alcohol. The yield by this method is very poor, only fifteen grams of bromide being obtained from eighty grams of alcohol, whereas Lieben and Rossi obtained one and a half grams of bromide for every gram of alcohol used. The tertiary butyl bromide was made by the action of bromine and red phosphorus on Kahlbaum's trimethyl carbinol, boiling at 83°–86°. The yield was poor, only seven grams of the bromide being obtained from one hundred grams of the alcohol.

The bromides were kept over calcic chloride in the dark. They were tested from time to time to determine whether or not they undergo spontaneous decomposition. The ethyl, propyl, butyl and isopropyl and ethylene bromides showed no evidence of any change. The isobutyl bromide, though at first neutral to test paper and containing no free bromine, contained after two months an amount of hydrobromic acid corresponding to a decomposition of 3.09 per cent. Three weeks later the decomposition had increased to 6.6 per cent., and 1.52 per cent. of the isoamyl bromide had decomposed. Both bromides remained perfectly colorless. Their boiling points had changed but slightly. They were carefully washed, dried, and subjected to fractional distillation. The fractions used were tested and found to contain no impurities, but, after a month, 4.03 per cent. of the isobutyl bromide had again decomposed. The tendency of isobutyl and isoamyl bromides to decompose spontaneously was observed, in alcoholic solutions of these compounds, by Remsen and Hillyer.[1] This property of these bodies throws doubt upon the utility of some of the data obtained from them. I shall call attention to this further on. The tertiary butyl bromide commenced to decompose after a few days. It was therefore, as the quantity was small, put into small bulbs which were sealed and kept in the dark. One of the bulbs was put into a bottle which was tightly corked and the bulb broken, as it seemed desirable to determine the relative amount of decomposition in contact and out of contact with the air. After three and a half months, 63.13 per cent. of that in contact with the air, and 51.99 per cent. of that in a bulb, had decomposed. As bromine, shown by its brown color, and isobutylene are formed in this decomposition, the difference observed may be due to the low "limit" of the decomposition in the bulb (owing to pressure, etc.) rather than to the specific action of the air. Roozeboom[2] noticed that this bromide turns yellow on standing and that its vapor begins to dissociate below 100°. As Eltekoff[3] observed the dissociation of the vapor of isobutyl bromide, it seems probable that the spontaneous decomposition of isobutyl, isoamyl and tertiary butyl bromides is of the same general nature as dissociation.

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[1] Ann. Chem. (Liebig) **158**, 150.

[2] Loc. cit. 161.

As secondary butyl bromide was needed to complete the list of butyl bromides, an attempt was made to prepare it. The method that suggested itself was the action of hydrobromic acid on the alcohol. It was thought that the reduction of ethylmethylketone would give the alcohol, and therefore this ketone was made by heating a mixture of calcium propionate and acetate. All attempts to reduce it to the corresponding alcohol failed. Its alcoholic solution was treated with metallic sodium, and its aqueous solution with sodium amalgam (1 per cent. and 2 per cent.), with zinc and sulphuric acid, and with tin and hydrochloric acid, but the ketone was recovered unchanged. The subject was not pursued further on account of lack of time and a desire to go on with the main investigation. There can be no doubt that the body I attempted to reduce is a ketone, and, though it was not analysed, its boiling point and method of preparation show that it is ethylmethylketone.

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[1] This Journal 8, 261.

[2] Ber. d. chem. Gesell. 14, 2396.

[3] Ibid. 8, 1244.

To determine the stability at low temperatures, the bromides were weighed in sealed bulbs, these put into bottles of about 250 cc. capacity, the solution of the reagent added, the bottles closed with well ground stoppers, the bulbs broken by shaking, the bottles allowed to stand the required time, and, excepting in the first experiments, the amount of bromine extracted determined by Volhard's method. As silver nitrate decomposes the bromides, ferric sulphate and ammonium sulphocyanate were first added and then titrated to disappearance of color. In the experiments at higher temperatures, bottles of 125 cc. capacity were used, and instead of glass stoppers, corks. These were tied down and paraffined. Otherwise the method was the same as at lower temperatures. The use of bulbs prevents loss from volatility of the bromides, and, as the bromide is not brought into contact with the reagent until the bulb is broken, the system may be brought to any desired temperature without any action taking place at a lower temperature. The only apparent disadvantage attending the use of bulbs is the difficulty of putting the same quantity of liquid in every bulb. It therefore seemed desirable to determine if the absolute amount of bromide used has any effect upon the relative amount of decomposition.

INFLUENCE OF QUANTITY OF BROMIDE.

Different quantities of ethyl bromide were dissolved in equivalent quantities of sodic hydrate solution, $\frac{n}{10}$, allowed to stand for the periods of time given below, and the amount of decomposition determined by the loss of alkalinity. The results are as follows:

Time in Hours.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
18.5	.5390	.044145	8.19
18.5	1.0570	.085089	8.05
16.5	.2954	.012208	4.13
16.5	.1430	.005995	4.19
16.5	.2457	.009265	3.77

The first two were not started at the same time as the others, but at a time when the laboratory was much warmer, hence the greater velocity of change. An inspection of these figures shows that though the results do not agree very well, the percentage of change is apparently independent of the quantity of bromide. As the alkaline solution changes on standing, portions of it were put into 250 cc. bottles, allowed to stand a day, and the amount of change found to depend upon the bottle used, not being the same in any two. As, if the amount of bromide decomposed is determined by loss of alkalinity, this difference vitiates the result, even if blanks are used, the direct determination of the bromine abstracted was tried, the method being that given on page 43.

Different quantities of ethyl bromide were dissolved in sodic hydrate, $\frac{n}{10}$, allowed to stand seventy-two hours, and the amount of bromine abstracted determined.

Quantity Used.	Quantity Decomposed.	Percentage of Change.
.7533	.126985	16.85
.4628	.076300	16.48
.6316	.107910	17.07
.3870	.064310	16.61

These results show that the quantity of bromide used is without influence on the percentage of decomposition.

To determine the relative stability of the bromides toward sodic hydrate, at ordinary temperatures, duplicates of each bromide in equivalent quantities of sodic hydrate solution, $\frac{n}{10}$, were allowed to stand for the periods given below.

RELATIVE STABILITY TOWARD SODIC HYDRATE.

Series I.

This series was allowed to stand one day.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2788	.051775	18.57
Ethyl,	.24225	.042946	17.72
Propyl,	.2688	.018327	6.82
Propyl,	.3298	.023739	7.19

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Butyl,	.2345	.014933	6.38
Butyl,	.2459	.015755	6.40
Isopropyl,	.2514	.004428	1.76
Isopropyl,	.3115	.004920	1.58
Isobutyl,	.23365	.005257	2.25
Isobutyl,	.2740	.008055	2.94
Isoamyl,	.3508	.012835	3.66
Isoamyl,	.2714	.010419	3.58
Ethylene,	.2040	.089206	43.73
Ethylene,	.1721	.075294	43.75
Tertiary butyl,	.1832	.15618	85.25

Series II.

This series was allowed to stand two days. As one of the bottles containing ethyl bromide was cracked in breaking the bulb, but one determination of ethyl bromide was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2469	.070959	28.74
Propyl,	.1654	.020418	12.34
Propyl,	.2769	.036531	13.19
Butyl,	.2131	.023975	11.25
Butyl,	.2020	.023016	11.39
Isopropyl,	.2200	.007011	3.19
Isopropyl,	.2212	.007011	3.17
Isobutyl,	.2182	.009274	4.25
Isobutyl,	.2247	.009348	4.16
Isoamyl,	.26015	.011627	4.47
Isoamyl,	.2442	.012684	5.19
Ethylene,	.1711	.084318	49.30
Ethylene,	.1833	.090240	49.23
Tertiary butyl,	.1315	.114943	87.41

Series III.

This series was allowed to stand four days. Only a single determination of ethyl bromide is given, as one of the bottles was accidentally broken.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2141	.081401	38.02
Propyl,	.1610	.033456	20.78
Propyl,	.1527	.031857	20.86
Butyl,	.1235	.022331	18.08
Butyl,	.1889	.035072	18.56
Isopropyl,	.1784	.008610	4.87
Isopropyl,	.1988	.009592	4.81
Isobutyl,	.2050	.011615	5.75
Isobutyl,	.1866	.010674	5.72
Isoamyl,	.1985	.017969	9.04
Isoamyl,	.2087	.019026	9.11
Ethylene,	.1917	.097290	50.75
Ethylene,	.1444	.073320	50.77
Tertiary butyl,	.1309	.118505	87.94

Series IV.

This series was allowed to stand seven days. During this period the temperature of the laboratory ranged from zero to 25°.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.5021	.232715	46.34
Ethyl,	.4847	.226185	46.66
Propyl,	.3648	.083025	22.75
Propyl,	.3378	.075645	22.39
Butyl,	.2786	.055211	19.80
Butyl,	.3520	.071788	20.39
Isopropyl,	.2725	.017712	6.50
Isopropyl,	.3551	.023001	6.47
Isobutyl,	.3231	.029866	9.24
Isobutyl,	.4699	.043840	9.32
Isoamyl,	.4341	.045300	10.43
Isoamyl,	.3740	.039160	10.46
Ethylene,	.4319	.223720	51.10
Ethylene,	.5206	.266020	51.09
Tertiary butyl,	.2173	.191800	88.27

Series V.

This series was allowed to stand fourteen days. The range of temperature was about the same as in Series IV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2005	.138757	69.20
Ethyl,	.1473	.101588	68.96
Propyl,	.2473	.106026	42.87
Propyl,	.2462	.105780	42.96
Butyl,	.2172	.078638	36.20
Butyl,	.2148	.082200	38.22
Isopropyl,	.2192	.032964	15.08
Isopropyl,	.1720	.028290	16.04
Isobutyl,	.2006	.035620	17.76
Isobutyl,	.2209	.038360	17.37
Isoamyl,	.2949	.063420	21.50
Isoamyl,	.2629	.058739	22.38
Ethylene,	.3711	.190820	51.42
Ethylene,	.4447	.228420	51.36
Tertiary butyl,	.1695	.157139	92.70

Series VI.

This series was allowed to stand twenty-eight days. The range of temperature was the same as in Series IV and V.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.4251	.346947	81.61
Ethyl,	.1819	.146823	80.71
Propyl,	.2066	.121647	58.85
Propyl,	.4224	.251781	59.60
Butyl,	.2688	.147275	54.78
Butyl,	.2227	.122752	55.11
Isopropyl,	.2616	.059778	22.85
Isopropyl,	.3579	.079335	22.17
Isobutyl,	.4309	.106723	24.76
Isobutyl,	.3791	.092886	24.50
Isoamyl,	.3021	.096187	31.83
Isoamyl,	.3583	.119592	33.87
Ethylene,	.5117	.266720	52.13
Ethylene,	.3221	.167252	51.92
Tertiary butyl,	.1697	.151248	89.12

Series VII.

This series was allowed to stand sixty-three days. Only one determination of each bromide was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.1882	.167315	88.90
Propyl,	.3914	.296922	75.86
Butyl,	.2667	.190841	71.59
Isopropyl,	.3784	.146493	38.71
Isobutyl,	.4443	.174812	39.34
Isoamyl,	.3254	.160513	49.35
Ethylene,	.3625	.189410	52.28

In order to render a comparison of these results as easy as possible, I have gathered them into one table which I have put on the following page. The figures at the heads of the columns indicate the time in days, and the results are given in per cents. Wherever two determinations were made their mean is given.

Summary.

Bromide.	1 day.	2 days.	4 days.	7 days.	14 days.	28 days.	63 days.
Ethyl,	18.14	28.74	38.02	46.50	69.08	81.16	88.96
Propyl,	7.00	12.71	20.82	22.57	42.91	59.18	75.86
Butyl,	6.39	11.32	18.32	20.10	37.21	54.93	71.59
Isopropyl,	1.67	3.18	4.84	6.48	15.60	22.51	38.71
Isobutyl,	2.60	4.20	5.74	9.28	17.57	24.63	39.34
Isoamyl,	3.62	4.83	9.08	10.45	21.89	31.85	49.35
Ethylene,	43.74	49.27	50.76	51.09	51.39	52.02	52.28
Tertiary butyl,	85.25	87.41	87.94	88.27	92.70	89.12	not determined.

We notice that up to a certain point, peculiar to each, ethylene and tertiary butyl bromides decompose very rapidly, but that as soon as this point is reached the decomposition proceeds very slowly. As the decomposition, however, progresses beyond this point, the phenomenon can scarcely be due to the establishment of equilibrium between the reacting bodies and the products of the reaction. It appears more probable that these bromides are entirely decomposed, and that other organic bromides, difficultly decomposable, are among the products. This view is strengthened by the fact that the "critical" point in the case of the ethylene bromide is the point at which half the bromine has been abstracted by the sodic hydrate. This corresponds to the formation of vinyl bromide, $C_2H_4Br_2 + NaOH = C_2H_3Br + NaBr + H_2O$; and Wislicenus[1] has shown the stability of vinyl compounds. The decomposition of the other bromides appears to be normal and regular. Their relative stability is, in order of increasing stability, ethyl, propyl, butyl, isoamyl, isobutyl, and isopropyl. To determine if this order of stability remains constant with increasing concentration, suitable quantities of the bromides were dissolved in $\frac{n}{5}$ sodic hydrate solution, and allowed to stand at the temperature of the laboratory one, two and four days.

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[1] Annalen **212**, 246.

Series VIII.

This series was allowed to stand one day.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3962	.136359	34.42
Propyl,	.4732	.056949	15.20
Butyl,	.3841	.041100	10.70
Isopropyl,	.5122	.013898	2.69
Isobutyl,	.5575	.022300	4.00
Isoamyl,	.5094	.028841	5.66
Ethylene,	.2816	.136278	48.39
Tertiary butyl,	.2489	.209610	84.21

Series IX.

This series was allowed to stand two days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3484	.150747	43.27
Propyl,	.4589	.096678	21.06
Butyl,	.2672	.051238	19.17
Isopropyl,	.3699	.018849	5.09
Isobutyl,	.4281	.025772	6.02
Isoamyl,	.3906	.035089	8.98
Ethylene,	.2621	.132258	50.45
Tertiary butyl,	.2349	.200842	85.54

Series X.

This series was allowed to stand four days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3286	.190602	58.00
Propyl,	.3829	.124476	32.50
Butyl,	.2567	.075213	29.30
Isopropyl,	.3320	.028167	8.48
Isobutyl,	.3885	.036287	9.34
Isoamyl,	.3672	.053209	14.49
Ethylene,	.2341	.120602	51.51
Tertiary butyl,	.2437	.214268	87.94

Leaving ethylene bromide, for reasons already given, out of consideration, we see that the relative stability is not affected by changing the concentration of the solutions. We find that the isobromides are more stable toward sodic hydrate than the normal bromides, which in turn are, if we may draw any conclusion from the one example studied, more stable than the tertiary bromides. Isopropyl bromide, a secondary bromide, is the most stable of those investigated. On trying to find the connection between the formulæ and the relative stability of the bromides, we see that the group $(CH_3)_2\overset{|}{C}H$ apparently exerts a restraining influence on the bromine. The bromides containing this group are comparatively stable. Comparing their formulæ, $(CH_3)_2CHCH_2CH_2Br$, $(CH_3)_2CHCH_2Br$ and $(CH_3)_2CHBr$, we observe that as the bromine "approaches" the "protecting" group it becomes more fixed. Further investigation of the subject is required before it can be stated that the group $(CH_3)_2\overset{|}{C}H$ does really "protect" the bromine. The action of other reagents seems to indicate that it does not, but that we have here merely a coincidence.

Comparing stability and molecular weight, we find that the stability of normal bromides increases while that of isobromides decreases with increasing molecular weight.

Having now determined the relative stability toward sodic hydrate, the action of other reagents was tried. The solutions of ammonia, potassic hydrate, nitric acid, sulphuric acid and silver nitrate described on pages 40 and 41 were used.

ACTION OF AMMONIA.

The first experiments upon the action of ammonia were made by heating to 60° for one hour, but, owing to pressure, several of the bottles broke and the series is incomplete.

Series XI.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3080	.005450	1.77
Propyl,	.2716	.003444	1.27
Isopropyl,	.3397	.000861	.25

The experiments were therefore repeated at zero. The series was allowed to stand one hundred and forty-five hours in a vessel containing melting ice. The results obtained are as follows:

Series XII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.7544	.002834	.37
Propyl,	.7039	.002091	.29
Isopropyl,	.7106	.000246	.034
Isobutyl,	.5358	.022742	4.22[1]
Isoamyl,	.6643	.008909	1.34
Ethylene,	.4418	.000188	.042

The amount of change was determined by estimating by Volhard's method the quantity of bromine abstracted, and, as the products of the reaction are ammonium bromide and alkyl ammonium bromides, it became necessary to ascertain if the latter hold their bromine in such a way that it can be determined by this method. Investigation proved that the bromine is so held. This and the slowness of action of ammonia on alkyl bromides indicate a re-arrangement in the formation of alkyl ammonium bromides, and are opposed to the view that these are molecular compounds, for were they molecular compounds they would be formed quite rapidly and the bromine combined in the same way as in the alkyl bromides, and not capable of determination by Volhard's method.

ACTION OF POTASSIC HYDRATE.

These experiments were made by allowing the solutions to stand at zero for one hundred and forty-five hours.

Series XIII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.7920	.137040	17.29
Propyl,	.7299	.046740	6.40
Isopropyl,	.8881	.011193	1.26
Isobutyl,	.4765	.026304	5.52[1]
Isoamyl,	.5599	.019781	3.53
Ethylene,	.4442	.185180	41.68

These results show that the order of stability toward potassic hydrate is the same as toward sodic hydrate. As a series[2] of experiments upon the action of sodic hydrate at zero was undertaken at the same time as Series XII and XIII, I have thought it desirable to compare the percentage results obtained. At the top of each column is the name of the alkali used.

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[1] 4.03 per cent. due to spontaneous decomposition.

[2] Series XVIII.

Comparison of Results.

Bromide.	Sodic Hydrate.	Potassic Hydrate.	Ammonia.
Ethyl,	15.20	17.28	.37
Propyl,	7.02	6.40	.29
Isopropyl,	1.44	1.26	.034
Isobutyl,	1.65[1]	1.49[1]	.19[1]
Isoamyl,	3.86	3.53	1.34
Ethylene,	40.96	41.68	.042

We see that the ratio between the action of these alkalies on the bromides is not constant, but depends upon the bromide used. As Ostwald has shown that this ratio, in the case of bases acting upon acids, is independent of the acid used, it is probable that the variability noticed above is due to secondary action. It shows that the reactions between alkyl bromides and alkalies are not applicable to determinations of the relative affinity of bases. Reicher[2] obtained similar results on comparing the action of sodic and baric hydrates on acetic ethers, as the coefficients thus obtained do not bear a constant ratio to each other. Ammonia acts very slowly on the bromides. Its action upon ethylene bromide is particularly striking, as, compared with sodic or potassic hydrate, it decomposes but one one-thousandth as much of this compound, which, unstable toward the others, is very stable toward it. The comparatively great decomposition of the isoamyl bromide may be due to the instability of its solutions. This source of error was determined in the case of the isobutyl bromide, and the figures given in the table have been corrected. In the experiments upon the action of potassic hydrate and ammonia, butyl and tertiary butyl bromides were omitted, as the quantity of each at my disposal was small and needed for other experiments.

ACTION OF ACIDS.

Preliminary experiments having shown that the bromides are decomposed very slowly by nitric and sulphuric acids at ordinary temperatures, the solutions, after standing eight days at the temperature of the laboratory, were heated to 60° for twelve hours.

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[1] Corrected.

[2] Ann. Chem. (Liebig) **232**, 106.

ACTION OF NITRIC ACID.

Series XIV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3375	.082513	24.48
Propyl,	.2817	.035793	12.70
Butyl,	.1714	.017810	10.39
Isopropyl,	.2408	.054858	22.78
Isobutyl,	.3043	.017536	5.76
Isoamyl,	.2865	.028539	9.96
Ethylene,	.3109	.001692	.54
Tertiary butyl,	.1646	.106723	64.84

ACTION OF SULPHURIC ACID.

Series XV.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3977	.086437	21.73
Propyl,	.2079	.021156	10.17
Butyl,	.2083	.021641	10.38
Isopropyl,	.2673	.075030	28.06
Isobutyl,	.1656	.009179	5.54
Isoamyl,	.4436	.039411	8.88
Ethylene,	.3274	.001880	.57

We see that the relative stability toward acids is not the same as toward bases. Ethylene bromide, so unstable with potassic and sodic hydrates, is hardly attacked by acids; and isopropyl bromide, so stable with alkalies, is, when treated with nitric acid, the most unstable of the bromides, and is easily attacked by sulphuric acid. With nitric acid, as with alkalies, the relative stability of normal bromides increases and that of primary isobromides decreases with increasing molecular weight. With sulphuric acid, however, propyl bromide is more stable than butyl bromide, but the difference is very slight and may be due to experimental error. The action of nitric and sulphuric acids upon the alkyl bromides is complicated by their action upon the alcoholic solvent. To determine the extent of this secondary action, vials containing some of the acid solutions were treated in the same way as Series XIV and XV and the loss of acidity determined. This amounted to 5.88 per cent. in the nitric acid and 24 per cent. in the sulphuric.

ACTION OF SILVER NITRATE.

Silver nitrate, both in neutral and in acid solution, was allowed to act upon the bromides. The solutions were kept in the dark twenty-two hours and the unchanged silver nitrate determined.

Series XVI.

Bromide.	Qnantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3874	.187698	48.68
Propyl,	.3138	.106146	33.82
Butyl,	.2541	.082474	32.45
Isopropyl,	.2451	.228919	92.99
Isobutyl,	.3030	.028907	9.54
Isoamyl,	.2522	.065987	26.16
Ethylene,	.2813	.005076	1.80

With silver nitrate, as with acids, ethylene bromide is very stable and isopropyl bromide very unstable. Compared with other reagents, silver nitrate acts rapidly on most of the bromides. The order of stability of ethyl, propyl, butyl, isobutyl, and isoamyl bromides is the same as toward nitric acid and sodic and potassic hydrates.

ACTION OF SILVER NITRATE AND NITRIC ACID.

To determine the action of silver nitrate in acid solution, the solution of silver nitrate and nitric acid described on page 41 was used. The conditions were the same as in Series XVI.

Series XVII.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2363	.123606	52.30
Propyl,	.2940	.132963	45.19
Isopropyl,	.3728	.368016	98.71
Isobutyl,	.3301	.036990	11.17
Isoamyl,	.3421	.098602	28.81
Ethylene,	.2845	.006298	2.21

The order of stability is the same as in neutral solution, but the amount of change is in all cases greater. As the action of nitric acid alone, under the same conditions, is almost inappreciable (less than .1 per cent.), the increased amount of change cannot be due to its specific action upon the alkyl bromides, but indicates the increased activity of silver nitrate in acid solution.

INFLUENCE OF TEMPERATURE.

The influence of temperature on chemical action, though universally recognised since the time of Bergmann, forms, as Ostwald says, "the subject of one of the darkest chapters in chemical mechanics." Wilhelmy, in 1850, attempted to give a mathematical expression for the influence of temperature on the velocity of a reaction. Since then Berthelot,[1] Harcourt and Esson,[2] Warder,[3] and Hood[4] have proposed formulæ, but they are applicable only to special cases. Van't Hoff[5] and Reicher[6] have applied a formula proposed by the former, and found the results calculated to agree with those obtained. Urech[7] has deduced and applied a formula differing slightly from that of Van't Hoff. All the chemists mentioned, as well as Fleurie,[8] Ostwald,[9] Menschutkin,[10] and Sabatier,[11] have studied the subject experimentally, but, though many interesting facts have been brought to light by this happy combination of theory and experiment, we are still far from the goal, and it will probably be many years before we have a general formula for expressing the influence of temperature on all chemical reactions. Van't Hoff[12] has indeed said that "the influence of temperature on the velocity of change depends upon the reaction chosen for consideration"; and Ostwald,[13] in his work on the action of acids on acetamide, found that the ratio between the velocity coefficients at 65° and at 100° varies with the acid used. Urech[14] observed similar phenomena in studying the inversion coefficients of acids. It was therefore considered necessary to study the influence of temperature upon the stability of the alkyl bromides, in order to determine if the variations are sufficient to change the order of stability. The reaction with sodic hydrate was chosen for this purpose. A $\frac{n}{10}$ solution was used throughout and, as in the experiments at ordinary temperatures, the bromides were dissolved in equivalent quantities of this solution.

To determine the influence of temperature it is necessary to compare the so-called "velocity coefficients." As is readily seen, the ratio between the amounts changed at two temperatures in one hour will differ from the corresponding ratio in two hours. For if in one hour at the temperature t 50 per cent. of the compound used is decomposed, and at the temperature t' 10 per cent., in the next hour 50 per cent. and 10 per cent. respectively of the remainders will be decomposed, and therefore in two hours 75 per cent. and 19 per cent. The ratios are in one hour 50 : 10 or 5 : 1, and in two hours 75 : 19 or about 4 : 1. Therefore some function must be compared which is independent of the time chosen. The velocity of a chemical change depends, other things being equal, upon the quantities of the reacting bodies and upon a constant which is a function of the nature of these bodies. This may be expressed in an irreversible reaction by the equation

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[1] Ann. chim. phys. [3], 68.

[2] J. Chem. Soc. **20**, 492.

[3] This Journal **3**, 347.

[4] Phil. Mag. [5], 6.

[5] Etudes de dynamique chimique, 112.

[6] Ann. Chem. (Liebig) **232**, 113.

[7] Ber. d. chem. Gesell. **16**, 762.

[8] Ann. chim. phys. [5], **7**, 391.

[9] J. prakt. Chem. [2], **27**, 26.

[10] Ibid. [2], **29**, 437.

[11] C. R. **106**, 63.

[12] Etudes de dynamique chimique, 117.

[13] J. prakt. Chem. [2], **27**, 26.

[14] Ber. d. chem. Gesell. **16**, 762.

$$\frac{dx}{dt} = K(A - x)(B - x),$$

in which K represents the constant, or velocity coefficient, A and B the molecular quantities of the reagents a and b, and x the amount of change. As, if we use equivalent quantities of a and b, A and B become equal, we may write the equation $\frac{dx}{dt} = K(A - x)^2$. Integrating we get, as t and x reduce to zero together, $\frac{x}{A - x} = AKt$. As this formula can be applied only to irreversible reactions, it became necessary to prove that the reaction studied is not a reversible reaction. For this purpose the action of sodic bromide upon methyl, ethyl, propyl and amyl alcohols and ethylene glycol was studied. Sodic bromide, in the proportions of 10.3 grams and 103 grams to the liter, was heated with the alcohols themselves, with the alcohols to which ten per cent. of water had been added, and with dilute solutions of the alcohols in ethyl alcohol, with and without the addition of ether. Though heated in all these cases to 60° for twenty-four hours, the sodic bromide was not changed. The reaction, therefore, is not reversible. I have therefore used the equation $\frac{x}{A - x} = AKt$ to determine the value of K. The figures thus obtained show what the relative change would be if the "active masses" of the reagents could be kept constant throughout the reaction. They are inversely as the relative time required for the same amount of decomposition. As the figures are comparative, I have, in order to avoid small fractions, multiplied K by one hundred million. A has been chosen equal to one hundred. An ordinary water-bath was used in the preliminary experiments, but, as the temperatures of different parts were different, it was discarded. A drying oven with double walls, the space between being filled with water, was tried and discarded for the same reason. A water-bath of ten liters capacity, placed within a larger bath, was found to have the same temperature throughout and was therefore used. By means of a thermo-regulator the temperature of this bath could be kept constant to within two tenths of a degree. In the experiments at zero the bottles were entirely surrounded by water in which melting ice was kept. In the experiments at other temperatures they were allowed to float upon the hot water, and, as they were never full, about one third was above the surface of the water. Of course the pressure in the bottles varied with the temperature, but the velocity of reactions of this nature was found by Van't Hoff[1] and Berthelot[2] to be independent of the pressure.

STABILITY AT ZERO.

Series XVIII.

This series was kept at zero for one hundred and forty-five hours, hence t, which is the time expressed in minutes, is equal to eight thousand seven hundred.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	AKt.	K.
Ethyl,	.7299	.110962	15.20	.17924	20.6
Propyl,	.4184	.029397	7.02	.07550	8.68
Isopropyl,	.8188	.011808	1.44	.01461	1.68
Isobutyl,[3]	.5644	.009313	1.65	.01678	1.93
Isoamyl,	.7931	.030653	3.86	.04017	4.62
Ethylene,	.6101	.249946	40.96	.69376	79.7

STABILITY AT 30°.

Series XIX.

This series was heated to 30°. Duplicates of each bromide were used, one being heated for two hours, the other for three. In the column marked t I have given the time, in minutes, of each determination.

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[1] Etudes, 43.

[2] Ann. chim. phys. [3] **66**, 45.

[3] Tests applied immediately after starting this series showed that the isobutyl bromide had undergone partial decomposition. Therefore the result obtained was corrected and is given as corrected. As with my apparatus I could not keep a temperature between zero and thirty degrees constant, the next experiments were carried on at the latter temperature.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.3556	.026375	7.41	.08003	120	667
Ethyl,	.3315	.035643	10.75	.12044	180	668
Propyl,	.2588	.007011	2.71	.02785	120	232
Propyl,	.2772	.011088	4.00	.04166	180	233
Butyl,	.2865	.006166	2.15	.02197	120	183
Butyl,	.1777	.005691	3.20	.03306	180	184
Isopropyl,	.2254	.001728	.77	.00776	120	64
Isopropyl,	.2258	.002683	1.18	.01193	180	66
Ethylene,	.3395	.098408	28.98	.40805	120	3400
Ethylene,	.2452	.087591	35.74	.55742	180	3098

Excepting in the case of ethylene bromide, the duplicates agree so closely that there can be no doubt of the correctness of the formula used. Ethylene bromide acts abnormally.

STABILITY AT 40°.

Series XX.

This series was kept at 40°. Duplicates of each bromide were used, one being heated about one hour, the other about two. As two bottles, one containing ethylene, the other tertiary butyl bromide, were broken, but one determination of each of these bromides was made.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.3564	.033459	9.38	.10351	61	1697
Ethyl,	.3166	.054173	17.11	.20642	121	1706
Propyl,	.2049	.007503	3.66	.03799	60	623
Propyl,	.3030	.021402	7.06	.07596	120	627
Butyl,	.1975	.006165	3.12	.03220	61	528
Butyl,	.2116	.013152	6.21	.06621	122	542
Isopropyl,	.3708	.003690	.995	.01005	61	164
Isopropyl,	.2501	.004620	1.967	.02007	121	165
Isoamyl,	.2744	.005436	1.98	.02020	64	315
Isoamyl,	.3279	.011174	3.42	.03541	120	295
Ethylene,	.1541	.043710	33.85	.51156	60	8526
Tertiary butyl,	.1291	.125903	83.42	5.10873	60	85145

STABILITY AT 50°.

Series XXI.

This series was kept at 50°. Duplicates of each bromide were used, as in Series XX. Owing to the breaking of three bottles, one of which contained butyl bromide, and the others isobutyl and tertiary butyl, the series is incomplete.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*t.*	*K.*
Ethyl,	.1940	.043382	22.36	.28799	60	4800
Ethyl,	.2979	.110428	37.03	.58805	120	4900
Propyl,	.2699	.027183	10.07	.11197	60	1866
Propyl,	.2572	.045510	17.69	.21735	120	1811
Butyl,	.2067	.018632	9.01	.09901	60	1650
Isopropyl,	.2205	.006888	3.13	.03231	60	539
Isopropyl,	.3381	.020910	6.18	.06481	120	540
Isobutyl,	.2712	.021697	8.00	.08695	120	725
Isoamyl,	.3103	.017063	5.49	.05703	60	951
Isoamyl,	.2780	.028690	10.32	.11507	120	959
Ethylene,	.3138	.152562	48.61	.94590	60	15766
Ethylene,	.2009	.100837	50.09	1.00360	120	8363
Tertiary butyl,	.1272	.109874	86.38	6.34214	60	105702

STABILITY AT 60°.

Series XXII.

This series was kept at 60° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	*AKt.*	*K.*
Ethyl,	.4232	.184428	43.57	.77210	12868
Propyl,	.3868	.094956	24.55	.32538	5423
Isopropyl,	.2985	.026076	8.73	.09565	1594
Isobutyl,	.2260	.023534	10.41	.11619	1936
Isoamyl,	.3476	.039864	11.46	.12943	2157
Ethylene,	.2421	.123892	51.17	1.04792	17465

The results obtained in Series XVIII to XXII show that the order of stability of the alkyl bromides is the same at all temperatures between zero and 60°. In order that the influence of temperature upon the velocities of the reactions studied may be more readily seen, I have brought all the results into one table, below. The figures given are the values of the velocity coefficient *K.*

Summary.

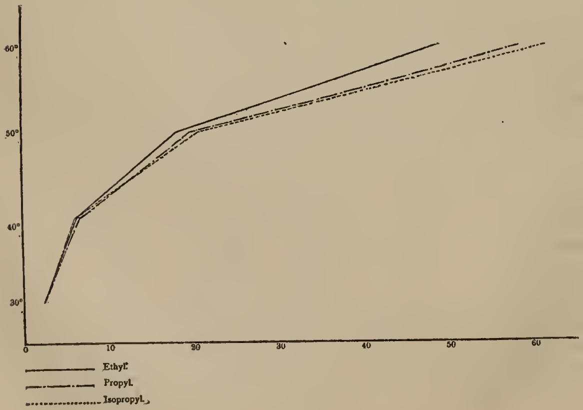
Bromide.	Zero.	30°.	40°.	50°.	60°.
Ethyl,	20.6	667	1702	4850	12868
Propyl,	8.68	232	625	1838	5423
Butyl,	...	183	535	1650	...
Isopropyl,	1.68	65	164	539	1594
Isobutyl,	1.93	...	...	725	1936
Isoamyl,	4.62	...	305	955	2157
Ethylene,	79.7	3551	8526	15766	17465
Tertiary butyl,	...	...	85155	105702	...

The figures obtained for ethylene are not the true values of K, as the reaction between sodic hydrate and ethylene bromide is not regular and normal. It is impossible at present to deduce the true values of K for this reaction. The same is probably true of tertiary butyl bromide. Comparing the velocity coefficients at 30°, 40°, 50°, and 60° with each other, we find that their ratios are, in the case of ethyl bromide, 1 : 2.55 : 7.27 : 19.44; in the case of propyl bromide, 1 : 2.69 : 7.92 : 23.37; and in the case of isopropyl bromide, 1 : 2.52 : 8.29 : 24.52.

These ratios, though showing a general resemblance, prove the truth of Van't Hoff's statement that "the influence of temperature varies with the reaction under consideration."

Interpolation formulæ of the general form $x = A + at - bt^2 + ct^3$ seem best adapted to express these results. Representing by U the velocity coefficients of the reaction between ethyl bromide and sodic hydrate, by V those of the reaction between propyl bromide and sodic hydrate, and by Z those of the reaction between isopropyl bromide and sodic hydrate, we get the following formulæ:

$$U = 667 + 92.824\theta - 3.702\theta^2 + .4758\theta^3.$$
$$V = 232 + 49.801\theta - 3.642\theta^2 + .2583\theta^3.$$
$$Z = 65 + 8.522\theta - .637\theta^2 + .0672\theta^3.$$
$$\theta = t - 30.$$



These formulæ can be applied only between 30° and 60°. Other formulæ are probably required for other ranges of temperature. The results obtained are graphically expressed by the foregoing cut. To admit of more easy comparison I have divided the velocity coefficients of ethyl bromide by 266.8, of propyl bromide by 92.8, and of isopropyl bromide by 26.

INFLUENCE OF LIGHT.

As the influence of light upon the velocity of reactions of this nature has never been studied, a series of the bromides in $\frac{n}{10}$ sodic hydrate was protected from light, but otherwise kept under the same conditions as Series VI, both being started at the same time.

Series XXIII.

This series was kept, in the dark, twenty-eight days.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.	Series VI.
Ethyl,	.2052	.167533	81.64	81.16
Propyl,	.2646	.158793	60.01	59.23
Butyl,	.3383	.186868	55.23	54.95
Isopropyl,	.3838	.081180	21.24	22.51
Isobutyl,	.2294	.057225	24.93	24.63
Isoamyl,	.4067	.133786	32.89	32.60
Ethylene,	.2175	.111202	51.12	52.02
Tertiary butyl,	.2065	.182758	88.49	89.12

I have put the results of Series VI in the last column. A comparison of this with the fourth column shows that light has no influence on the velocity of reactions of this nature.

EFFECT OF CONCENTRATION.

The velocity of a reaction between two bodies depends, if other conditions remain constant, upon the frequency of impact of the molecules, and therefore, theoretically, the amount of change in unit time is, in unit volume, as the square of the concentration, and, in unit mass, directly as the concentration. From this it follows that the amount of change referred to unit mass is the same in N hours in a solution of concentration C as in one hour in a solution of concentration NC. Van't Hoff[1] and Ostwald[2] found that these theoretical deductions hold good only if very dilute solutions are used, and that the extent to which the dilution must be carried varies with the reaction under consideration. The following experiments were therefore undertaken to determine how far the dilution must be carried in the reactions between sodic hydrate and alkyl bromides. The bromides were dissolved in $\frac{n}{10}$, $\frac{n}{20}$, $\frac{n}{40}$ and $\frac{n}{50}$ sodic hydrate solutions, which were then kept at 54° for one, two, four and five hours respectively.

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[1] Etudes, 25.

[2] J. prakt. Chem. [2] **31**, 307.

Series XXIV.

This series was kept at 54° for one hour. The solutions were $\frac{n}{10}$.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3063	.089698	29.28
Propyl,	.3014	.044526	14.77
Isopropyl,	.3522	.024477	6.95
Ethylene,	.3103	.152374	49.10

Series XXV.

This series was kept at 54° for two hours. The solutions were $\frac{n}{20}$.

Ethyl,	.2710	.090841	33.52
Propyl,	.2942	.053628	18.22
Isopropyl,	.2635	.019922	7.55
Ethylene,	.3644	.181702	49.86

Series XXVI.

This series was kept at 54° for four hours. The solutions were $\frac{n}{40}$.

Ethyl,	.2018	.081751	40.51
Propyl,	.3638	.072570	19.94
Isopropyl,	.4090	.039606	9.68
Ethylene,	.2805	.150964	53.82

Series XXVII.

This series was kept at 54° for five hours. The solutions were $\frac{n}{50}$.

Ethyl,	.2522	.101697	40.32
Propyl,	.2661	.054120	20.33
Isopropyl,	.2600	.024354	9.33
Ethylene,	.2880	.154348	53.82

Bringing the results of Series XXIV to XXVII together in one table, we get the following

Summary.

Bromide.	$\frac{n}{10}$ for one hour.	$\frac{n}{20}$ for two hours.	$\frac{n}{40}$ for four hours.	$\frac{n}{50}$ for five hours.
Ethyl,	29.28	33.52	40.51	40.32
Propyl,	14.77	18.22	19.94	20.33
Isopropyl,	6.95	7.55	9.68	9.33
Ethylene,	49.10	49.86	53.82	53.82

The differences between the figures in the last two columns are within the limit of experimental error; therefore, for dilutions beyond $\frac{n}{40}$ the velocity of change is inversely as the concentration.

INFLUENCE OF SOLVENT.

The specific influence of so-called "neutral" solvents was first noticed by Berthelot and Péan de St. Gilles,[1] who found that the velocity of etherification is less if ether is used as a solvent than if benzene is employed. Ostwald[2] found that the velocity of the action of acids on methyl acetate varies with the solvent, and Menschutkin,[3] in studying the velocity of etherification of alcohols by acetic anhydride, arrived at a similar conclusion. Ostwald used as solvents water, acetone, and methyl and ethyl alcohols; Menschutkin, benzene, hexane and xylene. I therefore thought it desirable to determine the effect of change of solvent upon the velocities of the reactions under consideration. For this purpose $\frac{n}{10}$ solutions of sodic hydrate were made by dissolving metallic sodium in methyl and propyl alcohols, containing about half a per cent. of water. Suitable quantities of the bromides were dissolved in these and the solutions kept at 54° for one hour. As Series XXIV was kept at the same temperature for the same length of time, the results thus obtained admit of comparison with the results of that series.

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[1] Ann. chim. phys. [3], 66, 66. [2] J. prakt. Chem. [2], 28, 457. [3] Zeits. phys. Chem. 1, 628.

Series XXVIII.

In this series the bromides were dissolved in equivalent quantities of $\frac{n}{10}$ solution of sodic hydrate in methyl alcohol. The series was kept at 54° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.3523	.059514	16.89
Propyl,	.2923	.023004	7.87
Butyl,	.2740	.021235	7.74
Isopropyl,	.3580	.010086	2.81
Ethylene,	.2971	.144760	48.72

Series XXIX.

In this series the bromides were dissolved in equivalent quantities of $\frac{n}{10}$ solution of sodic hydrate in propyl alcohol. The series was kept at 54° for one hour.

Bromide.	Quantity Used.	Quantity Decomposed.	Percentage of Change.
Ethyl,	.2492	.061149	24.53
Propyl,	.2583	.027180	10.52
Butyl,	.3049	.030825	10.11
Isopropyl,	.3251	.013653	4.19
Ethylene,	.3067	.150588	49.09

Summary.

Bromide.	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.
Ethyl,	16.89	29.28	24.53
Propyl,	7.87	14.77	10.52
Butyl,	7.74	14.01	10.11
Isopropyl,	2.81	6.95	4.19
Ethylene,	48.72	49.10	49.09

An inspection of this summary shows that the action is slower in methyl alcohol than in propyl alcohol, and slower in propyl alcohol than in ethyl alcohol. As part of the change may be expressed by the equation, $C_nH_{2n+1}Br + NaOH + C_mH_{2m+1}OH = C_nH_{2n+1}OC_mH_{2m+1} + NaBr + H_2O$, it remains an open question whether or not the "active" part taken by the alcohols in this reaction is the cause of the difference in velocity. The influence of the alcohols upon the rate of change does not bear a simple relation to their molecular weights, as the results obtained with propyl alcohol are intermediate between those obtained with methyl and ethyl alcohols as solvents.

EFFECT OF EXCESS OF REAGENT.

According to one of Guldberg and Waage's fundamental equations, $\frac{dx}{dt} = K(nA - x)(mB - x)$, the velocity of a reaction is similarly affected by a similar excess of either reagent. Urech,[1] in his studies on the action of Fehling's solution and dextrose, and of acetyl bromide and bromine, and Landolt,[2] in studying the reaction of sulphurous acid on iodic acid, found that an excess of one reagent produces a different effect on the velocity, from that produced by an excess of the other. Reicher,[3] in his researches on the saponification of ethyl acetate by sodic hydrate, and Hood, in his work on the oxidation of ferrous sulphate by potassic chlorate, found that a similar excess of either reagent has the same effect on the velocity. I have studied the effect of excess of reagent upon the reaction between sodic hydrate and ethyl bromide, using an excess of each reagent under similar conditions, so that the results admit of direct comparison. They are as follows:

Series XXX.

In this series, which was kept at 53° for one hour, ethyl bromide, in $\frac{n}{10}$ solution, was treated with one half, one, two and three equivalents of sodic hydrate.

	Quantity Used.	Quantity Decomposed.	Percentage of Change.	$NaOH : C_2H_5Br$.
Ethyl bromide,	.5501	.186764	15.77	½ : 1
" "	.5207	.146387	28.11	1 : 1
" "	.3023	.135923	44.96	2 : 1
" "	.2514	.141700	56.36	3 : 1

Series XXXI.

In this series, which, like Series XXX, was kept at 53° for one hour, sodic hydrate, in $\frac{n}{10}$ solution, was treated with one half, one, two and three equivalents of ethyl bromide.

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[1] Berichte **17, 18, 19**.

[2] Berichte **19**, 1317.

[3] Annalen **228**, 257; and **232**, 103.

	Quantity Used.	Quantity Decomposed.	Percentage of Change.	$C_2H_5Br : NaOH$.
Sodic hydrate,	.2046	.032286	15.78	½ : 1
" "	.1910	.053691	28.11	1 : 1
" "	.2039	.090777	44.52	2 : 1
" "	.1287	.072124	56.04	3 : 1

The differences in the fourth columns fall within the limit of experimental error, and we may therefore conclude that in this reaction similar effects are produced by similar excess of either reagent.

Comparing all the results obtained, we see that toward sodic or potassic hydrate, nitric acid, silver nitrate, or silver nitrate and nitric acid, the stability of normal bromides increases, and that of primary isobromides decreases, with increasing molecular weight. This order of stability is probably the same toward all reagents, as the slight deviation from it when sulphuric acid is used falls within the limit of error, and the apparent instability of isoamyl bromide toward ammonia is probably due to spontaneous decomposition. We may therefore conclude that that factor of the stability which is a function of the molecular weight is constant with all reagents. This is not true of that factor which is a function of the constitution. Secondary propyl bromide is more stable toward alkalies, but less stable toward other reagents, than the primary bromide. The dibromide studied is less stable toward fixed alkalies than the monobromides, but more stable toward other reagents. As the order of stability of isopropyl, isobutyl, and isoamyl bromides varies with the reagent, and as, excepting with alkalies, isoamyl bromide occupies the intermediate position, it follows that the group $H\overset{|}{C}(CH_3)_2$ exerts its influence only upon the alkalies, or that the "protection" noticed is merely a coincidence. Further investigation is needed to decide this question. Though the spontaneous decomposition of tertiary butyl bromide prevents any great value being attached to the data obtained for the action of reagents on this compound, there can be no doubt that this bromide is very unstable toward alkalies.

JOHNS HOPKINS UNIVERSITY, *June*, 1888.

REVIEWS AND REPORTS.

ON RAOULT'S METHOD FOR THE DETERMINATION OF MOLECULAR WEIGHTS.

As is well known, the need of a method for determining the molecular weights of compounds which cannot be converted into vapor has long been felt. Such a method appears now to be at our disposal in that proposed by Raoult,[1] which is based upon observations on the depression of the freezing point of solvents by substances in solution. In view of the importance of the method to chemistry, it appears that a brief account of the investigations bearing upon it may be of interest and profit to the readers of this Journal, and accordingly the following paper has been prepared at the suggestion of the editor.

Although published by Raoult in 1883, and in a number of subsequent papers quite fully developed, the method referred to did not attract the attention of chemists generally until the present year. In February last, Victor Meyer,[2] in an article calling attention to its value, characterised it as the most significant contribution to the list of physical processes applicable to chemical investigations since the discovery of the law of Dulong and Petit. This statement, based upon an investigation carried on in his laboratory by Auwers[3] to determine the value and limitations of the method, resulted in arousing the chemical world to its importance. Since then a number of investigators have applied it to various problems of interest, with such success that confidence in its accuracy has rapidly increased, until it may now fairly be said to have taken a permanent place in chemistry.

As early as 1788, Blagden[4] investigated the effect of dissolved salts upon the freezing point of water, and found that the depression was proportional to the concentration of the solution. In 1861, Rüdorff[5] rediscovered this principle, and specially investigating some apparent deviations from the law, found that these could be explained on the assumption of the formation of hydrates, and deduced a formula for determining whether in any solution of a given salt, hydrates are formed, and the amount of water thus combining with the dissolved substance. Ten years later, Coppet,[6] using solutions containing salts dissolved in quantities proportional to their molecular weights, discovered that salts of analogous constitution produced the same depression of the freezing point. In 1883, Raoult[1] investigated the application of this law to solutions of a large number of organic substances in water, with remarkable results. Dividing the observed depression of the freezing point for each substance by the weight dissolved in 100 grams of water, he obtained a coefficient of depression which, multiplied by the molecular weight of the substance as obtained by other methods, gave approximately the same quantity. This constant he termed the molecular depression. If C represent the depression in degrees centigrade, P the number of grams of substance dissolved in 100 grams of water, and M the molecular weight of the substance,

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[1] Ann. chim. phys. [5] **20**, **28**. [6] **2**, **4**, **8**; Compt. rend. **94**, **95**, **97**, **101**, **102**, **103**, **104**; Ztschr. phys. Chem. **1**, 186.

[2] Ber. d. chem. Ges. **21**, 536.

[3] Ber. d. chem. Ges. **21**, 701.

[4] Phil. Trans. Lond. 1788, p. 277.

[5] Ann. der Phys. Pogg. **114**, 63; **116**, 55; **145**, 599.

[6] Ann. chim. phys. [4] **28**, 366; **25**, 502; **26**, 98.

$\frac{C}{P} = A$, the coefficient of depression of the substance, and

$MA = T$, the molecular depression of the solvent.

T is constant not only for solutions of different concentration, but also has approximately the same value for all substances of analogous structure in the same solvent. Raoult therefore proposed to make use of this constant in determining the molecular weight of substances to which the vapor-density methods are not applicable. With a view to developing and perfecting this method, he carried on a series of experiments,[2] using other solvents, as benzene, nitrobenzene, ethylene bromide, formic acid, glacial acetic acid, thymol, and naphthalene, for each of which a different value was found for T. Comparing these values, he found that the depression caused by one molecule of any substance dissolved in 100 molecules of either solvent was very nearly constant, varying between 0.59° and 0.65°, the mean being 0.63°.

In this general form, however, the law is not applicable to the determination of molecular weights. Some solutions give depressions of the freezing point which seem to indicate that the molecules of the substance are doubled in solution; others show irregularities which must be accounted for by assuming partial dissociation. If, however, the molecular depression caused in a given solvent by a substance of known molecular weight is determined, this constant may be used in determining the molecular weight of any substance of similar composition, from the observed depression which it causes in the freezing point of the same solvent. The results thus obtained show a maximum variation of 10 per cent. from the accepted molecular weight, while in most cases the agreement is much closer; so that by observing proper precautions[3] in the application of this method, it can lead to no error in choosing between the multiples of the empirical formula.

[1] Ann. chim. phys. [5] **28**, 133.

[2] Ann. chim. phys. [6] **2**.

[3] V. Meyer, Ber. d. chem. Ges. **21**, 536; Auwers, same, p. 701.

Of the solvents used,[1] only water, benzene, and acetic acid can find general application. The molecular depression varies greatly for different classes of substances, so that its use is to be avoided where the substance to be examined is soluble in either of the other solvents. It is, however, possible, by properly determining the value of *T* which should be used, to secure accurate results with water. Benzene, though showing more uniform values of *T*, gives quite irregular results with some organic compounds containing the group OH. Acetic acid is the only solvent in which *T* has but one value for all substances, ranging between 36 and 40, with a mean value of 39. The following values of *T* have been carefully worked out by Raoult:

Water	19.	Most organic substances.
	35.	Salts of monovalent metals with monobasic acids.
	40.	“ “ “ “ dibasic “
	45.	Salts of divalent metals with strong monobasic acids.
	17.	“ “ “ “ dibasic acids.
Benzene	25.	Alcohols, acids, phenols.
	49.	Other organic compounds.
Acetic acid (glacial)	39.	All substances.

In no case should a solvent be chosen which can enter into chemical union with the substance to be examined.

The application of the method presents no serious difficulties and calls for no special skill in manipulation. The apparatus required is ready at hand in most laboratories. Except in the study of those substances which exhibit variations of the general law, very satisfactory work may be done with a thermometer graduated to tenths of a degree, a large test-tube and a beaker. Of the forms of apparatus described by recent investigators,[2] perhaps the most satisfactory is that proposed by Beckman[3] and shown (slightly modified) in the cut. A small battery-jar *A* is provided with a loosely fitting cover having a small hole *B* near the edge, through which passes a rod or stout wire *C*, bent at the lower extremity into a horizontal ring, to be used in stirring the freezing mixture. In the centre of the cover a large test-tube *D* is fastened, providing an air-space between the freezing mixture and the vessel containing the solvent. *E* is a test-tube having a capacity of about 25 cc. below the large side neck *F*, which serves for the introduction of the substances to be examined. Through the cork in *E*, in addition to the thermometer, a stout platinum wire works closely but freely. At the lower end this is bent into a horizontal ring for stirring. The thermometer, graduated to $\frac{1}{10}$ or $\frac{1}{20}$ degrees, is read with the aid of a lens or cathetometer, and estimated to hundredths of a degree.

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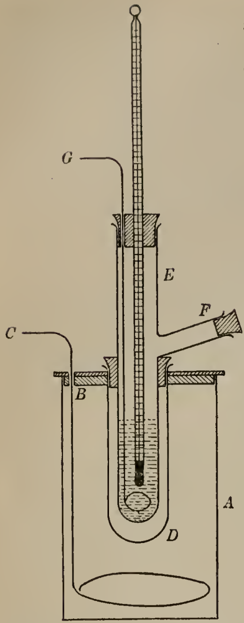
[1] Raoult, Ann. chim. phys. [6] **8**, 320; Paternò, Ber. d. chem. Ges. **21**, 3178; Beckman, Ztschr. phys. Chem. **2**, 715.

[2] Auwers, Ber. d. chem. Ges. **21**, 701; Ramsay, J. Chem. Soc. **54**, 621; Halleman, Ber. d. chem. Ges. **21**, 860.

[3] Ztschr. phys. Chem. **2**, 639.



To make a determination, tare *E*, and put in about 15 cc. of the solvent. Weigh to within a centigram. Put in a few small clippings of platinum foil, adjust the thermometer and insert in *B*. Cool down to half a degree or more below the freezing point of the solvent (as little below as possible will yield more accurate results), and by rubbing the platinum wire against the sharp edges of the foil, crystallisation is set up in the supersaturated liquid. The addition of a small crystal of the solvent is more often used for this purpose, but is less convenient and accurate. The thermometer rapidly rises, and within a few seconds becomes stationary, and remains so for a short time. As soon as this maximum is reached, the thermometer is read. Remove *E*, and thaw by placing in lukewarm water. Freeze again, and repeat until constant results are obtained. The second and third readings should not vary more than 0.02°, and if so, the last may be taken as the freezing point of the solvent. A weighed portion of the substance to be examined is then introduced, and the temperature read as before. Several successive portions may be introduced, increasing the concentration to any desired amount, and the molecular weight indicated at the various degrees of concentration may be calculated from the formula,

$$\text{Molecular weight} = \text{constant}\ \frac{\text{per cent. of substance in solution}}{\text{depression of freezing point}}.$$

The following examples will serve to illustrate the agreement of such results:

Glacial acetic acid.			Water.			Benzene.		
Per cent. of solution.	Depression.	Molecular weight.	Per cent. of solution.	Depression.	Molecular weight.	Per cent. of solution.	Depression.	Molecular weight.
Acetone$(CH_3)_2CO = 58$.			Acetone$(CH_3)_2CO = 58$.			Acetone$(CH_3)_2CO = 58$.		
0.502	0.340	57.6	0.662	0.220	56.9	0.473	0.405	57.2
1.776	1.175	58.9	2.416	0.770	59.3	1.458	1.220	58.6
4.402	2.835	60.6	6.221	1.930	60.9	4.592	3.615	62.2
9.202	5.785	62.0	12.35	3.820	61.1	7.162	5.365	65.4
12.48	7.775	62.8	18.52	5.660	61.8	12.27	8.470	71.0
15.91	9.740	63.7						

The more concentrated the solution the greater the depression, and therefore the less proportionate effect of an error in reading the thermometer. On the other hand, the separation of the first crystals of the solvent in freezing has, in concentrated solutions, a greater proportionate effect upon the concentration of the remainder, and prevents so great a rise in temperature upon freezing as would occur without this change in concentration; moreover, with a high degree of concentration the liquid must be cooled too far below its freezing point before crystallisation will begin. As a rule, an amount of substance in solution which will cause a depression of from one to two degrees has been found to give the most accurate results. This depends, however, upon the molecular depression of the solvent and the solubility of the substance examined.

With these precautions, it will be found possible to secure reliable results with substances which obey the general law. For those which show a coefficient of depression varying notably with the concentration of the solution, the work of Raoult and Beckman should be consulted.

A summary of some work of Brown and Morris[1] to determine the molecular weight of the carbohydrate raffinose, will convey a better notion of the value of the method. To determine whether the action of substances of this class in aqueous solution is normal, experiments were made with other carbohydrates, the molecular depression being taken at 19, as found by Raoult for organic substances in water.

		Calculated.	Mean found.
Dextrose,	$C_6H_{12}O_6$	180	180.2
Cane sugar,	$C_{12}H_{22}O_{11}$	342	337.5
" " after inversion,			174.3
Maltose,	$C_{12}H_{22}O_{11}$	342	322
Milk sugar,	$C_{12}H_{22}O_{11}$	342	345
Arabinose,	$C_5H_{10}O_5$	150	150.3

Having thus established the value of T for these compounds, raffinose was examined, with the following results:

Calculated for $C_{18}H_{32}O_{16}.5H_2O$.	Found mean,
594	528

indicating that the simplest empirical formula, and not a multiple of it, represents the true molecular weight.

Other recently published investigations bearing upon this method are the following: Raffinose, by Tollens and Meyer, Ber. d. chem. Ges. **21**, 1566; Oxides of nitrogen, by Ramsay, J. Chem. Soc. **54**, 621; Sulphur, bromine, iodine and phosphorus, by Paternò and Nasini, Ber. d. chem. Ges. **21**, 2153; Citraconic acid, by the same, Ber. d. chem. Ges. **21**, 2156; Fumaric and maleïc acids, by the same, Ibid.; Aluminium ethyl, by Roux and Louise, Compt. rend. **107,** 600, and Bull. soc. chim. Paris, **50,** 497; Nitriles, by E. von Meyer, J. prak. Chem. N. F. **38,** 339; On the method in general, by Arrhenius, Ztschr. phys. Chem. **2,** 491; and by Hentschel, Ibid. **2,** 306.

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[1] J. Chem. Soc. **54**, 610.

C. W. MOULTON.

NOTE.

The Atomic Weight of Tin.

Bongartz and Classen[1] have recently made a redetermination of the atomic weight of tin. They used four methods:

1. Oxidation of metallic tin by nitric acid;
2. Electrolysis of the salt $SnCl_4.2NH_4Cl$;
3. Electrolysis of the salt $SnCl_4.2KCl$;
4. Electrolysis of stannic bromide, $SnBr_4$.

Pure tin was made by starting with the purest Banca tin. This was converted into the tetrachloride, which was carefully fractionated. The pure liquid was treated with enough crystallised sodium sulphide to redissolve all the precipitated stannic sulphide, and after adding a quantity of a solution of pure sodium hydroxide equal to half the sodium sulphide used, and allowing to stand for a few days, the resulting liquid was subjected to electrolysis, when the tin was deposited as a silvery metallic powder. The tin thus prepared was found to be free from antimony. It was converted into the tetrachloride, and to this enough ammonium and potassium chlorides added to form the crystallised double salts, $SnCl_4.2NH_4Cl$ and $SnCl_4.2KCl$. These were carefully and frequently recrystallised. Another part of the tin was converted into the tetrabromide, and this fractionally distilled until pure. The results obtained by the four methods above mentioned are as follows:

By 1. Mean of 11 determinations, $Sn = 118.7606$;
By 2. " " 16 " $Sn = 118.8093$;
By 3. " " 10 " $Sn = 118.7975$;
By 4. " " 10 " $Sn = 118.7309$.

The 47 determinations give the mean value, $Sn = 118.7745$, with a difference between the maximum and minimum of 0.2485. The authors consider the results of methods 2 and 3 the most reliable, and the mean result of these gives, as the atomic weight of tin, $Sn = 118.8034$, which they adopt.

A. R. L. DOHME.

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[1] Ber. d. chem. Gesell. **21,** 2900.

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AMERICAN CHEMICAL JOURNAL.

INVESTIGATIONS ON THE SULPHON-PHTHALEÏNS.

I.—Sulphon-Fluoresceïn and Related Compounds.

By Ira Remsen and A. F. Linn.

Some results obtained by one of us (R.) and Hayes, in studying the action of resorcin upon a substance which we supposed to be ortho-sulpho-benzoic acid,[1] led us to undertake a revision of the work, in the hope that the subject might be cleared up. According to Remsen and Hayes, when resorcin and ortho-sulpho-benzoic acid are heated together, sulphon-fluoresceïn is obtained. The analyses of the product and of a barium salt obtained from it by boiling with barium carbonate, gave results which could not at the time be satisfactorily explained. On repeating the work, an observation was made at the outset which soon led to an explanation of the difficulties previously encountered. In making an analysis of the supposed ortho-sulpho-benzoic acid, it was found that a considerable amount of ammonia was given off from it on heating it with caustic potash. The substance had been prepared by heating benzoic sulphinide with concentrated hydrochloric acid in an evaporating dish on a water-bath, and had the properties ascribed to it by Remsen and Fahlberg[2] and by Brackett and Hayes.[3] Some of it further had been prepared by heating the sulphinide in a sealed tube with hydrochloric acid to 150°. In the first paper on this subject,[4] it was assumed that the action of hydrochloric acid upon the sulphinide takes place according to the following equation :

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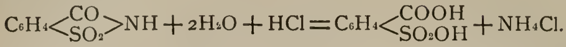
[1] This Journal **9**, 372.

[2] Ibid. **1**, 426.

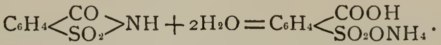
[3] Loc. cit.

[4] Loc. cit.



$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH + 2H_2O + HCl = C_6H_4<\begin{matrix}COOH\\SO_2OH\end{matrix} + NH_4Cl.$$

The product thus obtained was converted into the barium salt, and this into the acid potassium salt, and the latter was shown to be identical with the acid potassium salt of ortho-sulpho-benzoic, and the conclusion was drawn that the product is the free ortho-sulphonic acid. It appears, however, that this conclusion was erroneous, and that the substance is the acid ammonium salt of the acid, its formation taking place in accordance with the following equation:

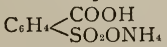


$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH + 2H_2O = C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix}.$$

This reaction takes place in a sealed tube in the presence of concentrated hydrochloric acid at 150°. The evidence of the correctness of this view is furnished by analyses and by the preparation of the acid ammonium salt directly from the free sulphonic acid.

The nitrogen was estimated by Kjeldahl's method, the ammonia driven over being determined by means of a dilute solution of sulphuric acid of such strength that 1 cc. contained 0.0475 gram H_2SO_4.

In seven analyses there were found respectively 6.12, 6.25, 6.57, 6.28, 6.24, 6.55 and 6.47 per cent. of nitrogen.

The calculated percentage of nitrogen for a substance of the formula  $C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix}$ is 6.39.

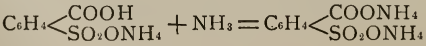
The neutralisation experiments gave the following results:

I. 0.2149 gram substance required for neutralisation 17.6 cc. of a solution of ammonia containing 0.0009508 gram to 1 cc.

II. 0.8073 gram required 66 cc. of the same solution of ammonia.

III. 0.1938 gram required 15.9 cc. of the solution of ammonia.

The weight of ammonia required for neutralisation according to the equation:



$$C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + NH_3 = C_6H_4<\begin{matrix}COONH_4\\SO_2ONH_4\end{matrix}$$

is 7.76 per cent. of the weight of the acid ammonium salt taken. The results of the experiments correspond to 7.78, 7.77 and 7.80 per cent. respectively.

A sulphur estimation made by Liebig's method gave the following result:

0.2512 gram of the salt gave 0.267 gram $BaSO_4$.

	Calculated for $C_6H_4{<}\begin{smallmatrix}COOH\\ SO_2ONH_4\end{smallmatrix}$.	Found.
S	14.61	14.60

These results show pretty conclusively that the substance is the acid ammonium salt, and, finally, all doubt was removed by preparing the salt from free ortho-sulpho-benzoic acid by half neutralising it with a solution of ammonia. The salt obtained in this way had all the properties of the compound under investigation. A sulphur estimation gave 14.43 per cent., while the calculated percentage is 14.61.

For the sake of comparison, some of the compound was made by heating benzoic sulphinide with concentrated hydrochloric acid to 150° in a sealed tube, and the product was found to be identical in all respects with that obtained by heating the sulphinide with concentrated hydrochloric acid on a water-bath.

Ortho-sulpho-benzoic acid, $C_6H_4{<}\begin{smallmatrix}COOH\\ SO_2OH\end{smallmatrix}$.—The free acid was made by boiling a solution of the acid ammonium salt with barium carbonate for about two days, or until ammonia was no longer given off, filtering, exactly precipitating the barium with dilute sulphuric acid, and evaporating to a very small volume. After several recrystallisations from water, the acid forms white needles. It is very easily soluble in water, and melts at a low temperature. A thorough investigation of the acid has since been made by A. R. L. Dohme in this laboratory, and the results will be published later. They leave no question in regard to the nature of the compound.

Action of Acid Ammonium Ortho-sulpho-benzoate on Resorcin.

On repeating the experiment of Remsen and Hayes, the same results were obtained. When the acid ammonium salt and resorcin are heated together at 178°–185° for several hours, yellow lustrous plates appear in the liquid, and the whole mass becomes a thick, nearly solid, yellow paste. By repeatedly boiling this product with animal charcoal, all trace of color was removed and the substance was no longer fluorescent. In its pure form it is perfectly white, and has a beautiful satiny lustre resembling that of benzoic acid. When deposited rapidly from a hot concentrated solution, it takes the form of small scales or plates. When crystallised slowly, it appears in colorless, transparent plates which are monoclinic. Analyses gave the following results:

I. 0.1054 gram substance gave 0.0735 gram $BaSO_4$ (Liebig's method).

II. 0.2736 gram substance gave 0.0011547 gram N (Kjeldahl's method).

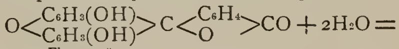
III. 0.3813 gram substance lost 0.0305 gram H_2O after heating for three to four hours at 125°–130°.

	Calculated for $C_{13}H_{13}O_6NS + 1\frac{1}{2}H_2O$.	Found.
N	4.14	4.22
S	9.47	9.57
H_2O	7.99	8.00

These results show that the substance is not sulphon-fluoresceïn, as it was supposed to be by Remsen and Hayes, but rather that the reaction takes place between one molecule of the acid ammonium salt and one molecule of resorcin. The product is the ammonium salt of a sulphonic acid of the formula

$$(HO)_2C_6H_3.CO.C_6H_4.SO_2OH,$$

or *dioxybenzoyl-benzene-sulphonic acid*, which is analogous to the dioxybenzoyl-benzoic acid obtained by Von Baeyer[1] by heating one part of fluoresceïn with three parts of caustic soda. The latter reaction takes place as represented in this equation:



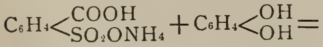
$$O{<}\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}{>}C{<}\begin{matrix}C_6H_4\\O\end{matrix}{>}CO + 2H_2O =$$

Fluoresceïn.

$$(OH)_2.C_6H_3.CO.C_6H_4.CO_2H + C_6H_4(OH)_2.$$

Dioxybenzoyl-benzoic acid. Resorcin.

The formation of the ammonium salt above described takes place according to the equation:



$$C_6H_4{<}\begin{matrix}COOH\\SO_2ONH_4\end{matrix} + C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} =$$

$$(OH)_2C_6H_3.CO.C_6H_4.SO_2ONH_4 + H_2O.$$

The product may be regarded as derived from the acid ammonium salt by replacement of the hydroxyl of the carboxyl by the resorcin-residue, $C_6H_3(OH)_2$.

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[1] Ann. Chem. (Liebig) **183**, 23.

Dioxybenzoyl-benzene-sulphonic acid, $(OH)_2C_6H_3.CO.C_6H_4.SO_2OH$.—In order to prepare the free acid, the ammonium salt was converted into the barium salt by boiling it in solution in water with barium carbonate, and the solution thus obtained was then treated with just enough dilute sulphuric acid to precipitate the barium. On evaporating the filtered solution to a small volume, the acid separated in small plates with a satiny lustre. It is extremely easily soluble in water both hot and cold. The solution is colorless, and gives no color with alkalies. When heated in an air-bath for several hours at 120° it loses water, partially fuses, and becomes yellow and finally dark brown. With alkalies, this dark brown substance gives an intense green-yellow fluorescence equal in intensity to that of fluoresceïn. It contains water of crystallisation, but owing to the fact that it is easily converted into the dark brown substance by loss of water, it is impossible to get a constant weight until this conversion is complete. The results obtained in estimating the sulphur show that the substance contains two molecules of water of crystallisation:

I. 0.1556 gram substance gave 0.1086 $BaSO_4 = 0.0149$ S (Pearson's method).

II. 0.2100 gram substance gave 0.1489 gram $BaSO_4 = 0.02045$ S (Pearson's method).

	Calculated for $C_{13}H_{10}O_6S + 2H_2O$.	Found.	
		I.	II.
S	9.70	9.58	9.74

The relation between the free acid and the ammonium salt obtained as the direct product of the action of resorcin upon acid ammonium ortho-sulpho-benzoate, was shown further by neutralising the acid with ammonia and evaporating to crystallisation, when a compound was deposited which had all the properties of the ammonium salt already described. The analyses gave the following results:

I. 0.2105 gram salt gave 0.1479 gram $BaSO_4 = 0.020313$ S (Pearson's method).

II. A determination of nitrogen by Kjeldahl's method gave 4.36 per cent. N.

III. 0.1092 gram substance lost 0.0088 gram H_2O after being heated for three hours at 135°–140°.

	Calculated for $C_{13}H_{13}O_6NS + 1\frac{1}{2}H_2O$.	Found.
N	4.14	4.36
S	9.47	9.65
H_2O	7.99	8.06

The *barium salt* made as above described, by boiling a solution of the ammonium salt with barium carbonate, first forms a dull red-colored solution, which on evaporation yields the salt in colored crystals. When recrystallised, however, it is obtained in large, transparent, light yellow, monoclinic plates. It is not very easily soluble in cold water, but readily in hot water. The water solution has a yellow color and shows an acid reaction. The analyses gave the following results:

I. 0.3329 gram salt gave 0.0936 gram $BaSO_4 = 0.05503$ Ba.

II. 0.2657 gram salt gave 0.0744 gram $BaSO_4 = 0.043745$ gram Ba.

III. 0.1846 gram salt gave 0.0517 gram $BaSO_4 = 0.0303987$ gram Ba.

IV. 0.2656 gram salt gave 0.0746 gram $BaSO_4 = 0.04386$ gram Ba.

V. 0.2656 gram salt, when heated for several hours at 170°–180°, lost 0.0339 gram H_2O.

VI. 0.3589 gram salt, when heated for several hours at 170°–180°, lost 0.046 gram H_2O.

	Calculated for $(C_{13}H_9O_6S)_2Ba + 6H_2O$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Ba	16.48	16.55	16.46	16.47	16.51	...	...
H_2O	12.99	...	...	...	...	12.76	12.82

Sulphon-fluoresceïn.

It was mentioned above that when dioxybenzoyl-benzene-sulphonic acid is heated for several hours at 120°, it is gradually converted into a dark brown substance which dissolves in alkalies, forming intensely fluorescent solutions. Von Baeyer has shown that when dioxybenzoyl-benzoic acid, or mono-resorcin-phthaleïn, as he calls it, is heated either alone or with resorcin, it is converted into fluoresceïn. It appeared highly probable, therefore, that the product obtained by heating dioxybenzoyl-benzene-sulphonic acid is the long-sought-for sulphon-fluoresceïn, and this it proved to be. The following method of preparation was found to yield entirely satisfactory results: 2 or 3 grams of the free acid are heated in a sulphuric acid bath to 185° for several hours, until the substance has acquired a dark brown color and water no longer comes off. The product is then treated with cold water and well washed. Afterwards it is dissolved in moderately concentrated caustic potash, and the solution filtered if necessary. Add dilute sulphuric acid and wash by decantation and finally on the filter with the aid of a pump, until all traces of potassium sulphate are removed. The pure substance thus prepared has a dark red-brown color.

Sulphon-fluoresceïn is difficultly soluble in hot water and in hot alcohol, but dissolves easily in the alkalies, giving intensely fluorescent solutions, and from these solutions it is precipitated by the addition of dilute acids. In some cases, on adding dilute sulphuric acid, the substance came out in yellow flocculent masses which quickly acquired a red-brown color.

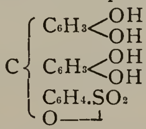
The analyses indicate that the substance has the composition represented by the formula, $C_{19}H_{12}O_6S + H_2O$, or $C_{19}H_{14}O_7S$.

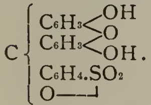
I. 0.0996 gram substance gave 0.0595 gram $BaSO_4 = 0.0082$ gram S (Pearson's method).

II. 0.1029 gram substance gave 0.0639 gram $BaSO_4 = 0.00878$ gram S (Pearson's method).

III. 0.0495 gram substance, when heated for one hour at 125°–130°, lost 0.0023 gram H_2O.

	Calculated for $C_{19}H_{12}O_6S + H_2O$.	Found.		
		I.	II.	III.
S	8.29	8.23	8.53	...
H_2O	4.66	...	...	4.65

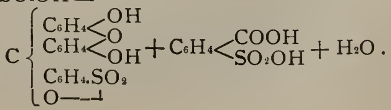
Whether the water given off is "water of constitution" or of crystallisation it is impossible to determine by the aid of the facts. The simplest view is that the compound has the structure represented by the formula  $C\left\{\begin{array}{l} C_6H_3<^{OH}_{OH} \\ C_6H_3<^{OH}_{OH} \\ C_6H_4.SO_2 \\ O\text{---}\lrcorner \end{array}\right.$, and that by loss of water it is converted into the anhydride analogous to fluoresceïn, viz.



$$C\left\{\begin{array}{l} C_6H_3<^{OH}_{O} \\ C_6H_3<_{OH} \\ C_6H_4.SO_2 \\ O\text{---}\lrcorner \end{array}\right. .$$

The conversion of dioxybenzoyl-benzene-sulphonic acid into sulphon-fluoresceïn by heat, probably takes place thus:

$$2(HO)_2C_6H_3.CO.C_6H_4.SO_2OH =$$

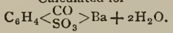


$$C\left\{\begin{array}{l} C_6H_4<^{OH}_{O} \\ C_6H_4<_{OH} \\ C_6H_4.SO_2 \\ O\text{---}\lrcorner \end{array}\right. + C_6H_4<^{COOH}_{SO_2OH} + H_2O .$$

When the product is dissolved in an alkali, a salt of the tetrahydroxyl compound is then probably formed, and from this the red-brown substance which was analysed is precipitated.

According to the equation just given, ortho-sulpho-benzoic acid should be contained in the water with which the sulphon-fluoresceïn was first washed. On boiling this solution with animal charcoal and evaporating to a small volume, a white substance which is very easily soluble in water, and resembles in every respect the acid already described, was obtained. A barium salt was made from it by boiling its solution with barium carbonate. This salt crystallises in bunches of transparent, radiating plates which closely resemble the barium salt of ortho-sulpho-benzoic acid. On analysis it gave the following results:

I. 0.1200 gram salt lost 0.0114 gram H_2O when heated for several hours at 210°; and then gave 0.0749 gram $BaSO_4 = 0.04404$ Ba.

	Calculated for  $C_6H_4<^{CO}_{SO_3}>Ba + 2H_2O$.	Found.
Ba	36.72	36.70
H_2O	9.65	9.50

The investigation of sulphon-fluoresceïn and related compounds will be continued in this laboratory.

Johns Hopkins University, 1888.

Communications from the Chemical Laboratory of Rutgers College.

XV.—ON HYPOCHLOROUS ACID IN ALKALINE SOLUTION.

By Peter T. Austen.

As is well known, hypochlorous acid is a very unstable substance and decomposes on small provocation according to the formula, $2HOCl = 2HCl + O_2$.

If an excess of hydrochloric acid is present, it is at once oxidised by the oxygen that is being liberated, and chlorine alone is set free: $2HOCl + 2HCl = 2H_2O + 2Cl_2$.

Hence, in treating hypochlorites with hydrochloric acid, chlorine is to a great extent obtained, unless the solutions are kept very dilute. On the other hand, if sulphuric acid is used to liberate the hypochlorous acid, the instability of the liberated acid soon causes its decomposition in solutions that are at all concentrated.

If, however, carbonic acid is used to decompose a hypochlorite, a curious condition of opposing affinities may arise. Carbonic acid is a slightly stronger acid than hypochlorous, and hence liberates it from its salts. When so liberated, the hypochlorous acid liberates its oxygen, and hence in this condition becomes of great value as a bleacher. On this property is founded the well-known bleaching method of Thompson, who passes goods through a dilute solution of chloride of lime and then hangs them in an atmosphere of carbonic acid. In this way all danger of free chlorine and its disastrous effects on fabrics is avoided.

It occurred to me that if a solution of chloride of lime were treated with sodium bicarbonate, a curious condition of electro-chemical conditions would arise; for the basic atom of hydrogen of the sodium bicarbonate must exchange with the calcium of the bleaching powder, forming sodium hypochlorite and calcium carbonate. The sodium atom of the sodium hypochlorite thus formed must again react with the basic hydrogen atom of another molecule of sodium bicarbonate, forming sodium carbonate and free hypochlorous acid.

(1). $Ca(OCl)_2 + NaHCO_3 = CaCO_3 + NaOCl + HOCl.$
(2). $NaOCl + NaHCO_3 = Na_2CO_3 + HOCl.$
$Ca(OCl)_2 + 2NaHCO_3 = CaCO_3 + 2HOCl + Na_2CO_3.$

I have not taken into account the calcium chloride in the bleaching powder, neither have I expressed the bleaching powder as $Ca(OH)(OCl)$, for the result in either case is the preliminary formation of sodium hypochlorite.

If the reactions are as above indicated, then we must have the somewhat paradoxical condition of a free mineral acid existing in a strongly alkaline solution. It was to be expected that when this solution of free hypochlorous acid in sodium carbonate was heated, the hypochlorous acid would decompose into hydrochloric acid and oxygen. The hydrochloric acid would act on the alkali carbonates and liberate carbonic acid. On heating, this took place. The liquid evolved gas which, after passing over caustic alkali to absorb the carbonic acid, was found to be oxygen.

A solution of sodium hypochlorite when boiled did not give off oxygen, but after passing through it a washed stream of carbonic acid, oxygen was evolved on boiling. The reaction is then,

$$2NaOCl + H_2CO_3 = 2HOCl + Na_2CO_3.$$

It is intended to try the effect of free hypochlorous acid in alkaline solution on organic substances.

I take pleasure in expressing my thanks to Mr. H. A. Smith, B. S., for efficient assistance rendered in this investigation.

XVI.—ON DI-AMIDO-SULPHOCYANBENZENE HYDRATE.

By Peter T. Austen.

By the action of dinitrobrombenzene on potassium sulphocyanide, dinitro-sulphocyanbenzene is formed.[1] This substance was placed in a flask with granulated tin and enough concentrated hydrochloric acid to cover the mass. On warming, an action began, which proceeded, under continued gentle application of heat, until the yellow sand had entirely disappeared and a colorless solution resulted. On evaporation of this solution, the tin salt crystallised out in transparent, shining needles, arranged in clusters of radiates about nuclei.

The salt was purified by recrystallisation from water, and analysed. The tin was precipitated as sulphide and weighed as di-oxide. The combustion was made with lead chromate, the front layer being of coarse cupric oxide.

	Calculated for $C_6H_3(NH_2)_2SCN(HCl)_2SnCl_2$.	Found. I.	II.
Sn	27.63	27.27	27.29
C	19.67	19.22	19.19
H	2.11	2.34	lost

An attempt was next made to prepare the hydrochloride of the base. To this end the tin was precipitated by hydrogen sulphide and the filtrate evaporated. The liquid soon discolored, showing decomposition. Evaporation in a vacuum and in a current of hydrogen also failed to yield the salt, decomposition taking place in both instances. The concentrated solution obtained by evaporation in a current of hydrogen deposited a few minute crystals on standing, but repeated experiments failed to afford any appreciable amount.

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[1] Austen and Smith, this Journal **8**, 89.

Not being successful in obtaining the hydrochloride, the preparation of the free base was next undertaken. The tin was precipitated from the acid solution obtained from the reduction, and the clear filtrate evaporated to a small volume in a current of hydrogen. It was then nearly neutralised with a 10 per cent. solution of caustic soda; the neutralisation being finished with a solution of sodium carbonate. A small amount of a blue decomposition-product which had been formed during the evaporation and neutralisation, was filtered off, the liquid concentrated by boiling, and allowed to stand. A fair crop of lavender-colored crystals was obtained.

The crystals were dissolved in hot water, and boiled with a little bone-black. The nearly colorless filtrate was allowed to stand. It deposited pinkish-gray needles of about $\frac{3}{16}$ inch in length. They carbonised without preliminary fusion at 180° (uncor.). Analysis gave:

	Calculated for $C_6H_3(NH_2)_2SCN.H_2O$.	I.	II.
C	45.90	46.20	...
H	4.92	5.50	...
N (absolute)	22.95	23.21	...
S[1]	17.48	17.45	17.26

I take pleasure in expressing my indebtedness to my assistant, Mr. Pennington Ranney, to whose skillful manipulation the success of this investigation is due.

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[1] The sulphur was determined by Carius' method, by oxidation with nitric acid. The sealed glass tube was placed in an iron one, and the space between them packed with pulverised barytes, such as is sold in the paint trade. This I found fully as good, if not better than the magnesia recommended by Warren (Chemical News **58**, 155). Barytes packs easily and firmly, is very fine and very cheap. The tubes so packed are relieved of all lateral strain, and stand 280° for hours. Explosion seldom occurs. The iron tube was not capped. Should explosion occur, the iron tube acts as a gun-barrel, and, in my laboratory, discharges its contents against a brick wall with no worse result than noise, odor and a slight fume. To screw on the cap as recommended by Warren, and so often done, does not seem to me to be advisable, as a serious explosion may result when the freedom of discharge is prevented.

ON THE BEHAVIOR OF PHENOL-PHTHALEIN WITH AMMONIA.

BY J. H. LONG.

The peculiar action of ammonia on phenol-phthalein was first pointed out by Beckurts, I believe, in a paper in the *Pharmaceutische Centralhalle.*[1] Soon after the experiments of Luck[2] were published, showing the great value of this substance as an indicator, it came into general use in Germany, and was even incorporated among the tests of a new edition of the German Pharmacopœia then published. Schlickum, in his Commentary on the German Pharmacopœia, 2d ed., states in one place that the behavior of litmus and phenol-phthalein in the titration of acids with ammonia water is the same, while in another place he remarks that the presence of ammonium salts interferes somewhat with the delicacy of the titration when phenol-phthalein is the indicator. Beckurts shows the error into which a number of writers had fallen in this regard, by giving a series of tests carried out with different indicators. In the following year, Flückiger[3] published experiments on the sensitiveness of phenol-phthalein, leading to the conclusion that it could not be employed with ammoniacal solutions. In the excellent papers by Thomson,[4] a similar conclusion is reached.

In the *Pharmacist*[5] I published the results of a long series of experiments on the action of phenol-phthalein, and among other points, I touched on the want of delicacy with ammonia. In that paper I offered an explanation of this behavior, suggested in part by a remark of Baeyer[6] on the formation of phenol-di-imido-phthalein, and partially confirmed this explanation by a number of experiments. Since then I have again taken up the subject, repeating the old experiments and adding new ones, which I think afford a full confirmation of my former suggestion. It is this later work which I wish to present here in detail.

When a few drops of an alcoholic solution of phenol-phthalein are added to a strong solution of soda, the deep red color which forms at first, vanishes in a short time—within a minute, if the soda

[1] 1883, p. 333.

[2] Ztschr. anal. Chem. 1877, 332.

[3] Ber. d. chem. Ges. **17**, 592. Ref.

[4] Chem. News **47**, 125, 135 and 184.

[5] 1885, 43; also Chem. News, **51**, 160.

[6] Ber. d. chem. Ges. **11**, 1297.

is sufficiently strong. The color can be restored by partial neutralisation with acids. When the indicator is added to strong ammonia solution (26 per cent.), a red color is produced which is more permanent, fading completely only after hours or days.

In this case, that is, after the *complete* disappearance of the color, addition of acid produces no change. If the acid is added before the color is fully discharged it becomes much brighter.

When phenol-phthalein is added to a very weak soda solution, the red color produced seems to be indefinitely permanent; but with weak ammonia it vanishes sooner or later, the interval between the mixing of the solutions and the disappearance of color depending on several factors, as dilution, temperature, and strength of indicator.

There are, therefore, important differences between the action of soda and that of ammonia on phenol-phthalein. If to a definite amount of a standard solution of hydrochloric acid containing a few drops of the indicator, standard ammonia solution be added, something more than the theoretical amount of the latter must be used to give the permanent red color. However, by increasing the amount of indicator added, or by cooling the solutions, the color can be obtained by nearly or quite the equivalent number of cc. of ammonia.

A similar result is obtained by adding soda solution to a solution containing, along with free mineral acid, some salt of ammonium and the indicator. The effect of temperature was shown by the following experiments. I prepared half normal solutions of hydrochloric acid and sodium hydroxide and a solution of ammonium chloride containing 100 grams in one liter. I took now 25 cc. of the acid, 10 cc. of the ammonium chloride, 65 cc. of water, and a few drops of the indicator. To the mixture, slightly less than 25 cc. of the sodium hydroxide was added, the whole was cooled to the desired temperature, and then more sodium hydroxide was run in to coloration. The results obtained at various temperatures are given in this table:

Temperature.	cc. $\frac{N}{2}$NaOH.	Temperature.	cc. $\frac{N}{2}$NaOH.
6.5	26.2	49.5	29.9
13.5	27.0	62.0	31.0
22.5	27.6	69.1	32.0
30.0	28.1	76.0	32.8
38.0	28.7		

The final reaction was in no case as sharp as in a titration between the alkali and acid alone, but the results are close approximations. Something similar is shown in the following experiments, which disclose likewise the effects of excess of ammonium chloride. Here I employed normal solutions of hydrochloric acid, sodium hydroxide, and ammonium chloride, and for each experiment took 25 cc. of acid, a definite quantity of ammonium chloride, and added enough water to make 100 cc. In each case 1 cc. of a one-tenth per cent. solution of phenol-phthalein was added, and then caustic soda from a burette to coloration.

The solution in the beaker was kept at a temperature of 0° C., and that in the burette as near this as possible. The experiments were repeated for each mixture three times, and gave closely agreeing results, the end reactions being quite satisfactory and sharp. In the following table the mean of the results from the three tests is given:

No.	HCl. cc.	NH_4Cl. cc.	H_2O. cc.	NaOH req'd. cc.
1	25	5	70	25.
2	25	10	65	25.08
3	25	15	60	25.20
4	25	25	50	25.28
5	25	30	45	25.37
6	25	50	25	25.68

These experiments show clearly that with the temperature sufficiently low, the disturbing action of small amounts of ammonium salts is very slight. They show also at what rate the disturbance increases with increasing amounts of ammonium chloride.

At a temperature of 20° C. I obtained the following results, working with the same solutions:

No.	HCl. cc.	NH_4Cl. cc.	H_2O. cc.	NaOH req'd. cc.
1	25	5	70	25.22
2	25	10	65	25.38
3	25	15	60	25.61
4	25	20	55	25.82
5	25	25	50	25.98

We find here differences in the amount of alkali required, varying between .2 cc. for the weakest solution to 1 cc. for that containing 25 cc. of ammonium chloride, which amounts to an error of 4 per cent. In all these cases the error is so large that it could not be neglected in any kind of practical work. However, by employing a larger amount of indicator, the error can be almost entirely corrected, as shown by the following tests:

I used here 25 cc. of the acid and 5 cc. of the ammonium chloride solution at a temperature of 20° C.

1. With 2 cc. of indicator required 25.12 cc. NaOH.
2. With 4 cc. of indicator required 25.02 cc. NaOH.
3. With 6 cc. of indicator required 25.00 cc. NaOH.

By using larger amounts of the indicator, the final reaction is obtained with satisfactory sharpness.

In another series of experiments, ammonia was run into the solution containing hydrochloric acid and different amounts of the phenol-phthalein. Where but a few drops of this were taken, the end reaction could not be observed accurately; with larger amounts the reaction was sharper, but only came after addition of an excess of alkali.

1. With 25 cc. of acid and 5 cc. of indicator I used 25.57 cc. of NH_4OH.
2. With 25 cc. of acid and 10 cc. of indicator I used 25.28 cc. of NH_4OH.

In presence of alcohol the reaction was always less distinct than with water, and more alkali was required to bring it.

The above results seem to indicate that ammonia combines with phenol-phthalein, forming, to some extent, a colorless compound, besides forming a colored one as does sodium hydrate; and also that this colorless body is produced more quickly as the temperature is higher or the ammonia stronger.

I expressed the opinion in my former paper, referred to above, that the phenol-di-imido-phthalein discovered by Baeyer is the compound formed here, and that this explains the peculiar reaction.

The experiments given below seem to confirm fully this view. Baeyer[1] states that phenol-phthalein and aqueous ammonia heated to 160°–170° in sealed tubes for some hours react on each other in this way:

$$C_{20}H_{14}O_4 + 2NH_3 = C_{20}H_{16}N_2O_2 + 2H_2O.$$

The phenol-di-imido-phthalein is a colorless body soluble in alkalies without color, but which dissolves at a high temperature in acids with formation of an ammonium salt and phenol-phthalein:

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[1] Ber. d. chem. Gesell. **11**, 1297.

$$C_{20}H_{16}N_2O_2 + 2H_2O + 2HCl = C_{20}H_{14}O_4 + 2NH_4Cl.$$

I prepared the product by the following methods:

1. 3 grams of phenol-phthalein and 30 cc. of strong ammonia were heated during three hours in a sealed tube to 160° C. The tube was then opened and the contents neutralised with hydrochloric acid. This precipitated a gummy mass, which was washed thoroughly with water, and finally dissolved in 90 per cent. alcohol. The solution, after filtration through bone charcoal, was evaporated to dryness. The residue left was dissolved in a mixture of equal parts of benzene and alcohol. The solution was allowed to evaporate spontaneously, leaving a residue, which was heated to 120° C. to completely remove all traces of the solvent. The product then remained as a colorless mass of fine needle-shaped crystals.

2. 10 grams of phenol-phthalein were treated with 200 cc. of strong ammonia solution in a flask kept hot on a water-bath during fifteen hours; at the end of that time the solution was neutralised with hydrochloric acid, and an insoluble gummy mass formed was treated as under 1.

3. 10 grams of phenol-phthalein were dissolved in 200 cc. of strong ammonia water (26 per cent.) at the ordinary temperature of the room. The color formed at first disappeared in four days without application of heat. I then neutralised with hydrochloric acid, and obtained the same product as above, which was treated in the same manner.

The three substances so obtained appeared quite similar, and turned red when moderately heated in a porcelain dish, melting finally at a higher temperature. They dissolved in sodium hydroxide solution without color. When heated to 110° C. with hydrochloric acid they formed ammonium chloride and phenol-phthalein, as shown by various tests. They all dissolved in strong nitric acid with a marked yellow color, which disappeared on addition of alkali.

It is apparent, therefore, that the phenol-di-imido-phthalein can be formed at ordinary temperature as well as in a sealed tube at 160°, although the preparation of a large amount at the lower temperature would require a much longer time.

The combination between the free alkali and the trace used as indicator in a practical titration would naturally require but a very short time at the ordinary temperature.

The rapidity of liberation of ammonia from an ammonium salt by fixed alkali depends on the temperature, and hence the very slight disturbance of the reaction with the mixed solutions in the above experiments carried out at a low temperature. Addition of sodium hydroxide seems to aid the reaction with ammonia solution, as shown by experiments in which I added the phenol-phthalein to ammonia solution and then the sodium hydroxide from a burette. With half-normal solutions the color was lost in half an hour by mixing 25 cc. sodium hydroxide, 20 cc. ammonia and .2 cc. of the indicator. Similar results were obtained with other solutions.

The above experiments show that the phenol-phthalein can be used with ammonia by taking certain precautions, and they also suggest why the behavior of this alkali was not sooner recognised. By working at a low temperature with a sufficiently large amount of the indicator, it was shown that fairly sharp results can be obtained. However, as we have other good indicators, it may never seem necessary to take these precautions.

After the introduction of the phenol-phthalein as an indicator, some time elapsed before its extreme sensitiveness was realised, and undoubtedly more was then added to a solution than is now considered necessary. Under these circumstances the difference in behavior between soda and ammonia would scarcely be noticed, and it remained for later observers, working with less of the reagent, to detect the discrepancy.

I am greatly indebted to my assistant, Mr. Mark Powers, for help in the details of the above experiments.

CHICAGO, *April* 12, 1888.

CONSTITUTION OF ALLYL CYANIDE.

BY CHASE PALMER.

The ease with which an allyl haloid is converted into allyl cyanide by contact with potassium cyanide at ordinary temperatures would naturally lead to the conclusion that the reaction is as follows:

$$CH_2:CH.CH_2Br + KCN = CH_2:CH.CH_2CN + KBr.$$

Allyl cyanide, however, is readily converted by alkalies into solid crotonic acid. Kekulé and Rinne[1] have also observed that, by oxidation with chromic acid, allyl cyanide does not yield formic acid, but, like crotonic acid, $CH_3.CH:CH.COOH$, it yields only acetic acid. They conclude, therefore, that a further change is involved by the introduction of the nitrile group, and that the resulting allyl cyanide has the formula $CH_3.CH:CH.CN$.

Pinner[2] retains for allyl cyanide the formula $CH_2:CH.CH_2.CN$. He assumes the first product of the alkaline action to be β-crotonic acid, $CH_2:CH.CH_2.COOH$, which takes up water directly, forming β-oxybutyric acid, $CH_3.CHOH.CH_2.COOH$, and that the latter, losing the elements of water, yields solid crotonic acid, $CH_3.CH:CH.COOH$. This ingenious explanation Pinner retains in a subsequent paper upon the same subject.[3] Hoping to learn which of the two formulas represents the constitution of allyl cyanide, I have studied the product formed by the addition of bromine to allyl cyanide.

Allyl bromide was found to furnish the largest yield of allyl cyanide, so that it was used as the source of the cyanide. As it was necessary to prepare allyl bromide, the method recommended by Grossheintz[4] was used. No data concerning the yield being available, I describe the method as I used it. 155 grams of powdered potassium bromide were mixed in a distilling flask with 75 cc. concentrated sulphuric acid, diluted with an equal volume of water. The flask was heated in an oil-bath to about 110° C., when hydrobromic acid was rapidly evolved. 50 grams of allyl alcohol were now allowed to drop slowly from a drop-funnel into the mixture. The allyl bromide distilled over through a condenser, and was collected in a receiver containing cold water. Towards the end the temperature of the oil-bath was raised to 125° C. The distillate, having been washed with water and neutralised with sodium carbonate, was separated, dried over calcium chloride, and rectified by distillation. From 50 grams of allyl alcohol 60 grams of allyl bromide were obtained.

Allyl Cyanide.—Since allyl cyanide cannot be made by the aid of alcohol, it was prepared by allowing allyl bromide to remain several weeks in contact with a saturated aqueous solution of potassium cyanide at the temperature of the room. 100 grams of allyl bromide, 54 grams of powdered potassium cyanide, and 33 cc. of water were mixed in a bottle, which was then tightly stoppered, and allowed to remain, with frequent agitation.

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[1] Ber. d. chem. Ges. **6**, 386.

[2] Ibid. **12**, 2056.

[3] Ibid. **17**, 2007.

[4] Ibid. **12**, 369.

At first the allyl bromide rests at the bottom of the bottle, but in about two weeks this disappears, and a light oil rises and floats on the solution. At the end of four weeks the floating oily liquid was removed, dried over calcium chloride, and fractionated. 37 grams (66 per cent. theory) of allyl cyanide were thus obtained. Considerable isonitrile was also formed. A small quantity of allyl bromide was recovered. Allyl chloride and allyl iodide, by similar treatment for a period of five weeks, gave respectively 11 per cent. and 16 per cent. of the theoretical yield of allyl cyanide.

5 grams of allyl cyanide (boiling point 116° C.) were dissolved in an equal volume of dry carbon disulphide. 11.8 grams of bromine, dissolved in five volumes of dry carbon disulphide, were allowed to drop slowly upon the allyl cyanide, which was kept cold by ice. The temperature of the cyanide solution did not rise above 10° during the process. The bromine had been distilled from sulphuric acid, and kept over lime for several days before it was used. The addition of bromine was rapid at first, but was slow towards the end. As soon as the bromine color had disappeared, the carbon disulphide was removed by distillation in a vacuum without the aid of heat, and the residue was distilled under 13 mm. pressure (oil-bath at 130°). It distilled completely below 110°, suffering partial decomposition. After standing a week in a vacuum desiccator over sulphuric acid and paraffin, it was analysed, giving a result required for dibrombutyric cyanide.

0.1965 gram substance gave 0.3270 gram AgBr.

	Calculated for dibrombutyric cyanide.	Found.
Br	70.48 per cent.	70.79 per cent.

This dibrombutyric cyanide is a heavy oil, having a peculiar pungent odor. Its vapor attacks the nose and eyes, causing a smarting sensation.

Etherification of the dibrombutyric cyanide.

A solution of 12 grams of the dibromcyanide in 20 cc. of 90 per cent. alcohol was saturated with hydrochloric acid gas at 5° C. After standing in a cold place over night, hydrochloric acid gas was again conducted through the mixture. On pouring the mixture upon ice, a heavy oil separated. This was removed, dried over calcium chloride, and distilled in a vacuum, leaving a solid residue in the distilling flask. The oil proved to be αβ-dibrombutyric ether. It could not be completely purified by distillation, but it boiled in a vacuum at 104–105° C. Dibrombutyric ether obtained from αβ-dibrombutyric acid also boiled at 105° under the same conditions.

The solid residue in the flask was found to be αβ-dibrombutyramide, $CH_3.CHBr.CHBr.CONH_2$. It was washed with a little ether, and obtained pure by two crystallisations from boiling benzene. Dried to constant weight in a vacuum, it was analysed with the following result:

0.2099 gram substance gave 0.3228 gram AgBr.

	Calculated for $C_4H_7Br_2NO$.	Found.
Br	65.30 per cent.	65.41 per cent.

The amide is difficultly soluble in cold water; more readily in boiling water, from which it crystallises on cooling in flat plates. It is easily soluble in ether and alcohol. The amide crystallises from hot benzene in flat plates. The pure substance melts at 150°–151° C.

αβ-Dibrombutyric acid.

4 grams of the dibrombutyramide were sealed in a glass tube with 20 grams of hydrochloric acid saturated at 16° C. The tube was heated an hour in the steam-bath. On removing the tube and letting the mixture cool, ammonium chloride crystals separated out. Water was added, the mixture extracted with ether, and the ethereal solution dried over calcium chloride. On evaporating the ether, the solid residue was purified by recrystallisation from boiling benzene. It melts constantly at 85° C. Dried at 100°, an analysis gave the following result:

0.1424 gram substance gave 0.2191 gram AgBr.

	Calculated for $C_4H_6Br_2O_2$.	Found.
Br	65.04 per cent.	65.40 per cent.

A comparison of this acid with αβ-dibrombutyric acid obtained by Michael and Norton from crotonic acid,[1] shows that it is the same substance. It is very soluble in alcohol and ether. Michael and Norton found the melting point of the acid to be 87° C. when crystallised from ether.

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[1] This Journal 2, 13.

The small quantity of the acid at my disposal made the use of benzene necessary, the acid being much less soluble in benzene than in ether.

Nothing besides $\alpha\beta$-dibrombutyric ether and $\alpha\beta$-dibrombutyramide could be obtained from the dibromcyanide formed by the addition of bromine to allyl cyanide. The conclusion is therefore justified that allyl cyanide has the constitution represented by the formula $CH_3.CH:CH.CN$.

Several years ago, Würtz[1] observed that β-butylene is the principal product of the action of zinc methyl on allyl iodide in the presence of sodium:

$$2CH_2:CH.CH_2I + Zn(CH_3)_2 = 2CH_3.CH:CH.CH_3 + ZnI_2.$$

The analogous intramolecular change which occurs in the formation of allyl cyanide, $CH_3.CH:CH.CN$, from allyl bromide, $CH_2:CH.CH_2Br$, further illustrates the tendency towards a symmetrical arrangement of atoms in the molecule.

Tufts College, Mass., *July*, 1888.

Contributions from the Chemical Laboratory of Harvard College.

LXII.—ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.[2]

By C. Loring Jackson and W. S. Robinson.

In an earlier paper from this laboratory,[3] the preparation of tribromtrinitrobenzol and its action with ammonia and aniline were described, and the announcement was made that the study of the behavior of this very reactive body would be continued. G. D. Moore and one of us accordingly have taken up the action of sodium malonic ester upon it, in the hope of substituting for each of the bromine atoms the radical of malonic ester, $CH(COOC_2H_5)_2$, and obtaining in this way a substance which might have yielded interesting derivatives. As, however, an entirely different product was the result of the reaction, it seemed wiser to study it with the much more accessible tribromdinitrobenzol, which acted in the same way, and to confine the work on the trinitro compound, which at best can be obtained only with difficulty, to those points in which the two substances showed a different behavior. In this paper, therefore, we give the results obtained up to the present time from the action of sodium malonic ester on tribromdinitrobenzol, which we are obliged to publish now, although in some respects the work is not so finished as we could wish, because the departure of one of us from Cambridge will prevent us from continuing the investigation together.

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[1] Compt. Rend. **68**, 841.

[2] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[3] This Journal **10**, 283.

The most important of these results can be summarised briefly as follows. Sodium malonic ester, under the conditions used by us, removes from tribromdinitrobenzol only two atoms of bromine, one of which is replaced by the radical of malonic ester, the other by hydrogen, so that the formula of the product is

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2.$$

This substance shows marked acid properties, and, although of a pale yellow color itself, forms salts most of which are dark blood-red; of these the sodium salt was analysed, and its formula proved to be

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

The yellow copper salt was also analysed, but proved to be a somewhat complex basic salt. The bromine contained in the substance is easily removed by treatment with aniline, the product being

$$C_6H_2C_6H_5NH(NO_2)_2CH(COOC_2H_5)_2,$$

which also gives a blood-red sodium salt with a formula similar to that of the salt derived from the original substance, but the acid properties of the anilido compound are much less pronounced. When heated with strong hydrochloric acid, the bromdinitrophenylmalonic ester gives ethyl chloride and a new substance melting at 170°, but the determination of its composition must be postponed till a later paper.

Action of Sodium Malonic Ester on Tribromdinitrobenzol.

If an alcoholic solution of sodium malonic ester is added to tribromdinitrobenzol (melting point 192°) dissolved in ether, the first drop imparts to the ethereal solution a blood-red color, which increases in intensity as more of the solution of sodium malonic ester is added, and the liquid contains the sodium salt of a new substance which we prepared in the following way. To an ethereal solution of a weighed quantity of tribromdinitrobenzol we added an alcoholic solution of sodium malonic ester in the proportion of three molecules of the ester to one of the tribromdinitrobenzol. The following were found to be convenient proportions: 20 grams of tribromdinitrobenzol, 16 grams of malonic ester dissolved in 100 to 150 cc. of absolute alcohol and treated with 2.4 grams of sodium as sodic ethylate. It was not necessary to add the ester gradually, and there was no perceptible evolution of heat during the reaction. The mixture was allowed to stand in a corked flask at ordinary temperatures for three or more hours, and the dark blood-red liquid thus obtained filtered from the precipitate of sodic bromide which had been deposited, acidified with dilute sulphuric acid, which changed the dark red color to pale yellow, and filtered once more to remove the sodic sulphate formed. The filtrate was then distilled on the water-bath until most of the ether had passed over, when the residue in the flask deposited, as it cooled, crystals of the new substance mixed with a large quantity of unaltered tribromdinitrobenzol. The mother-liquor from these crystals was allowed to evaporate spontaneously, and left a red or yellow oil mixed with a small additional quantity of the crystals, which were separated from it, and the oil allowed to stand in an open dish for some weeks, when it deposited an additional quantity of the crystals. The crystals, whether obtained by cooling the hot alcoholic solution, or from the oil by long standing in the cold, were purified by dissolving them in a little hot alcohol, and adding a moderately strong aqueous solution of sodic hydrate (the common laboratory solution diluted with its own volume of water), which converted the new substance into its soluble sodium salt, but left the tribromdinitrobenzol unaltered; the red solution was then poured into a large quantity of water, and the tribromdinitrobenzol removed by filtration. If the solid crystals were treated directly with the aqueous solution of sodic hydrate, the tribromdinitrobenzol was left in a form which clogged the filter very badly, whereas when an alcoholic solution was used, as directed above, no difficulty was encountered in the filtration. The red filtrate was acidified with dilute sulphuric acid, and the precipitate purified by crystallisation from hot alcohol until it showed the constant melting-point 75°–76°. After being dried *in vacuo*, its composition was determined by the following analyses:

I. 0.2061 gram of the substance gave on combustion[1] 0.2910 gram of carbonic dioxide and 0.0602 gram of water.

II. 0.2013 gram gave 0.2827 gram of carbonic dioxide and 0.0511 gram of water.

III. 0.1975 gram gave 0.2780 gram of carbonic dioxide.[2]

IV. 0.1926 gram of substance gave 12.4 cc. of nitrogen at a temperature of 20° and a pressure of 740 mm.

V. 0.2214 gram of substance gave by the method of Carius 0.1036 gram of argentic bromide.

VI. 0.2005 gram gave 0.0937 gram of argentic bromide.

	Found.					
	I.	II.	III.	IV.	V.	VI.
Carbon,	38.51	38.30	38.38	...	...	...
Hydrogen,	3.24	2.83	...	...	...	...
Nitrogen,	...	...	...	7.17	...	...
Bromine,	...	...	...	...	19.91	19.88

These results agree about equally well with the numbers calculated for two different formulas, as appears by the following comparison:

	Calculated for $C_6HBr(NO_2)_2C(CO_2C_2H_5)_2$.	Found Mean.	Calculated for $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$.
Carbon,	38.71	38.40	38.51
Hydrogen,	2.72	3.03	3.21
Nitrogen,	6.94	7.17	6.91
Bromine,	19.85	19.89	19.75

The first of these formulas, in which the two atoms of bromine removed from the tribromdinitrobenzol have been replaced by the bivalent radical $=C(CO_2C_2H_5)_2$, seems at first sight the most probable, especially since W. H. Perkin, Jr., and others have observed the strong tendency of sodium malonic ester to react in this way; but although this is the only formula we have been able to find which explains easily the removal of two atoms of bromine in this reaction, we are inclined to reject it in favor of the second one, in which one atom of bromine has been replaced by the univalent radical $—CH(CO_2C_2H_5)_2$, and the other by hydrogen, for the following reasons:

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[1] Care must be taken to heat the substance very gradually, as it shows a tendency to explode in the combustion-tube

[2] The water was lost in this analysis.

First, the formation of a sodium salt is hard to reconcile with the first formula, unless, indeed, sodic hydrate was added to it,[1] giving

$$C_6HBr(NO_2)_2OHCNa(CO_2C_2H_5)_2;$$

but our analyses of the sodium salt, given later in this paper, prove that it contains no hydroxyl, and to make this proof more convincing we prepared the salt for one of our analyses from sodic ethylate, as the radical $C_2H_5O—$, which in this case would be added instead of hydroxyl, would make a very great difference in the percentage composition of the salt; but this preparation, like the others, gave on analysis numbers corresponding to the formula

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

Secondly, the ease with which the sodium salt is formed, and with which it is decomposed by an acid giving the original substance, militates against the first formula, as we can hardly suppose that a ring of carbon atoms, such as must be assumed in this formula, would break when treated with an alkali, and reunite under the influence of an acid in dilute solutions. Finally, we may add that the meta position of the bromine atoms replaced deprives the first formula of any support from analogy.[2] The principal objection to the formula

$$C_6H_2Br(NO_2)_2CH(COOC_2H_6)_2,$$

which we adopt, is that we cannot account as yet for the formation of such a substance by the reaction of sodium malonic ester on tribromdinitrobenzol. We hope, however, that a careful study of the quantitative conditions of the reaction, and of the oil which is the secondary product, will throw light on this part of the subject; but owing to the departure of one of us from Cambridge, its further investigation must be postponed till next autumn.

The yield was far from satisfactory; 14 grams of tribromdinitrobenzol after treatment with 12 grams of malonic ester and 1.7 gram of sodium, as described above, giving only 4.3 grams of the bromdinitrophenylmalonic ester instead of the 14 grams required, if the whole of the tribromdinitrobenzol was converted into the new substance, that is, 30.7 per cent. of the theoretical yield. A large amount of the tribromdinitrobenzol was recovered, however, amounting to 5.5 grams, or 39.3 per cent. This leaves 30 per cent. unaccounted for, which probably remains dissolved in the oil deposited by the alcoholic mother-liquors; but that the dissolved substance is bromdinitrophenylmalonic ester admits of great doubt, as we have not succeeded in obtaining any considerable quantity of this substance from the oil by treatment with aqueous sodic hydrate. This point will be investigated more thoroughly hereafter. We have tried several modifications of the process, in hopes of improving the yield, but none of them have given satisfactory results; if, for instance, the proportion of sodium malonic ester is increased in order to bring more of the tribromdinitrobenzol into the reaction, any gain from this cause is more than compensated by the larger amount of the product taken up by the greater quantity of oil, which is only in part deposited on long standing. Nor was the yield increased by longer standing, or by boiling the materials with a reverse condenser; in this latter case the product came down in an oily form, and with, if anything, rather a smaller yield, was much harder to purify.

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[1] Wislicenus, Ann. Chem. **242**, 23.

[2] Compare J. Stanley Kipping, Ber. d. chem. Ges. **21**, 32.

Properties of the Bromdinitrophenylmalonic Ester, $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$.

The substance crystallises in pale yellow flattened needles, or long plates terminated by a single plane, which forms with the sides angles not very far from 90°, but distinctly obtuse and acute. It melts between 75° and 76°, and shows a tendency to explode at high temperatures, so that the heat must be applied carefully when making a combustion of the substance. It is not very soluble in cold alcohol, but freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in ether, benzol, or glacial acetic acid, even more so in chloroform; moderately soluble in acetone or carbonic disulphide, nearly insoluble in ligroine or water. Strong sulphuric acid in the cold has little action on it, although perhaps a small quantity dissolves; on warming the mixture, complete solution takes place, and addition of water precipitates a solid, which seems to consist principally of unaltered bromdinitrophenylmalonic ester mixed with a small amount of a substance with a higher melting point, probably the compound formed by the action of concentrated hydrochloric acid in sealed tubes (see page 104). Nitric acid, either strong or fuming, dissolves the bromdinitrophenylmalonic ester in the cold, but does not produce any change of color. In this respect it differs markedly from the corresponding trinitro compound. If the acid solution is warmed, decomposition seems to take place.

The bromdinitrophenylmalonic ester possesses well-marked acid properties, as was to be expected, since it contains a hydrogen atom standing between the two carboxyls of the malonic ester and a phenyl, which, as Victor Meyer[1] has shown, frequently exercises a negative influence, much heightened in this case by the presence of the two nitro groups. Sodic hydrate in either aqueous or alcoholic solution at once converts it into a soluble red sodium salt, and the same salt is formed by an alcoholic solution of sodium malonic ester, by sodic carbonate dissolved in water, or by acid sodic carbonate mixed with very dilute alcohol. The aqueous solution of the salt is, however, entirely decomposed by carbonic dioxide, the original substance being precipitated. An aqueous solution of the sodium salt prepared by treating an excess of the original substance with a solution of sodic hydrate, gave precipitates with salts of all the common metals except those of the alkalies. Most of these precipitates were red, and among them the following were especially characteristic:

Baric, strontic, or calcic chloride, dark brick-red.

Magnesic sulphate, rust color.

Zincic acetate, dark chrome-orange.

Basic plumbic acetate, very dark brick-red.

The neutral plumbic acetate gave a yellow precipitate, which turned white when in contact with an excess of lead salt.

Cupric sulphate, dark golden yellow.

Ammonic hydrate also dissolved the substance with a red color, but the salt was decomposed on trying to evaporate off the excess of ammonia on the water-bath, leaving a whitish residue, which seemed to consist principally of the original substance, with a small amount of decomposition product. The substance is in fact easily decomposed by either ammonic or sodic hydrate, and our rather unsatisfactory observations on these reactions will be found on page 104. The sodium salt boiled under a reverse condenser with ethyl bromide in alcoholic solution, passed from red through purple, bluish green, green and brown to reddish yellow; sodic bromide was formed, and the other product was an oily substance, which solidified after some time. It will be studied later. The bromine atom in the bromdinitrophenylmalonic ester seems to be removed with comparative ease. Up to this time, we have studied its behavior in this direction only with aniline (see page 102).

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[1] Ber. d. chem. Ges. **20**, 534; **21**, 1291 et seq.

The Sodium Salt, $C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was prepared by dissolving some of the bromdinitrophenylmalonic ester in alcohol and adding a little sodic hydrate, care being taken that the hydrate was not in excess; a little ether was then added, and the mixture evaporated rapidly in a small beaker sunk throughout its whole length in the water-bath. The ether vapor kept the air from coming in contact with the liquid while the alcohol was being heated to its boiling point. The residue, after all the alcohol had evaporated, was extracted with benzol to remove the excess of the ester, and then dried by gentle warming and standing *in vacuo* over paraffin and sulphuric acid. These precautions were adopted to avoid the contamination of the substance with the carbonic dioxide of the air. The same substance was obtained when sodic ethylate was used instead of sodic hydrate, and Analysis III was made with a sample prepared in this way.

I. 0.1950 gram of the substance ignited with sulphuric acid gave 0.0324 gram of sodic sulphate.

II. 0.1354 gram gave 0.0216 gram of sodic sulphate.

III. 0.1943 gram gave by the method of Carius 0.0838 gram of argentic bromide, and the filtrate gave 0.0330 gram of sodic sulphate.

IV. 0.2148 gram gave 14.3 cc. nitrogen at a temperature of 25° and a pressure of 759.6 mm.

	Calculated for $C_6H_2Br(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.			
		I.	II.	III.	IV.
Sodium,	5.39	5.38	5.16	5.50	...
Bromine,	18.74	...	...	18.35	...
Nitrogen,	6.55	...	...	...	7.42

The results of these analyses show that the substance is the normal salt, containing but one atom of sodium, and the important bearing of this point on the determination of the formula of the bromdinitrophenylmalonic ester has been discussed already. (See page 97.)

Properties.—The salt forms a dark blood-red powder, easily soluble in water, alcohol, or ether. From a solution containing much sodic hydrate, the salt can be extracted with ether; but pure water, on the other hand, extracts the salt from its ethereal solution. Its aqueous solution is decolorised by carbonic dioxide, bromdinitrophenylmalonic ester being precipitated.

The *copper salt* seemed from its appearance to promise excellent results on investigation, and was accordingly prepared as follows. An alcoholic solution of the bromdinitrophenylmalonic ester was treated with a small quantity of sodic hydrate, taking care that the ester was in large excess, and then poured into a volume of water sufficient to precipitate all the unaltered ester; after filtering, an alcoholic solution of cupric chloride was added, and the precipitate washed first with 50 per cent. alcohol, then with water, and finally once with hot alcohol; it was then dried *in vacuo*. It is not necessary to protect the salt from contact with the air during its preparation, as it is not perceptibly affected by carbonic dioxide. It gave the following results on analysis:

I. 0.2052 gram of the salt was treated according to the method of Carius and gave 0.0844 gram of argentic bromide. The filtrate was freed from argentic nitrate, and the copper precipitated by electricity from a sulphuric or nitric acid solution, giving 0.0197 gram of copper.

II. 0.2073 gram treated in the same way gave 0.0864 gram of argentic bromide and 0.0198 gram of copper.

III. 0.1455 gram gave 0.0138 gram of copper.

	Calculated for $HOCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$.	Found. I.	II.	III.
Copper,	9.36	9.60	9.55	9.48
Bromine,	17.70	17.50	17.74	...

From these results it would appear that the substance is a basic salt, or, at least, that it is not the normal salt, and in spite of its very promising appearance is not fitted to throw light on the nature of the original substance. We have not thought it worth while, therefore, to examine it more carefully. We may add that the salt changes color from a lighter to a darker yellow soon after it is prepared, which we are inclined to ascribe to the conversion of

$$ClCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$$

into the corresponding hydroxyl compound by the action of the water in which it is suspended.

Properties.—The copper salt forms an obscurely crystalline precipitate of a golden yellow color, with a very slight greenish tinge. It is essentially insoluble in water, alcohol, or ether, and is a comparatively stable substance, as it seems to be unaltered by exposure to the air or by heating to 100°. Strong nitric acid, even in excess, decomposes it, setting free the bromdinitrophenylmalonic ester.

Anilidodinitrophenylmalonic Ester,

$C_6H_5NHC_6H_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was made by mixing the bromdinitrophenylmalonic ester with aniline in the proportion of one molecule of the ester to two of the base. The solid becomes yellow almost immediately, and the action has come essentially to an end after the mixture has stood for a few minutes in the cold. As a measure of precaution, however, we always heated it gently for a few minutes, to make certain that all the bromine had been removed. The product was purified by crystallisation from alcohol, until it showed the constant melting point 118°, dried at 100°, and analysed.

I. 0.2104 gram of the substance gave on combustion 0.4262 gram of carbonic dioxide and 0.0903 gram of water.

II. 0.1886 gram of the substance gave 16.9 cc. of nitrogen at a temperature of 22° and a pressure of 766.6 mm.

	Calculated for $C_6H_2(NHC_6H_5)(NO_2)_2CH(CO_2C_2H_5)_2$.	Found. I.	Found. II.
Carbon,	54.68	55.24	...
Hydrogen,	4.56	4.77	...
Nitrogen,	10.07	...	10.24

Properties.—The anilidodinitrophenylmalonic ester forms flattened needles terminated by one or two planes, which form much more oblique angles with the sides than those which appear in the bromdinitrophenylmalonic ester. It is also found occasionally in star-shaped groups of needles, has a bright yellow color, and melts at 118°. It is only slightly soluble in cold alcohol, much more soluble in hot, but not freely even in this. More soluble in methyl than in ethyl alcohol; soluble in ether, or in carbonic disulphide; freely soluble in benzol, glacial acetic acid, or acetone, very freely in chloroform; essentially insoluble in water or ligroine. The best solvent for it is alcohol. Concentrated hydrochloric acid does not dissolve or act on it in open vessels, either hot or cold. An aqueous solution of sodic hydrate acts on it in the cold only very slowly and imperfectly, but gives a red solution when boiled with it. In alcoholic solution, sodic hydrate converts it into a red soluble salt; the anilido compound therefore still possesses acid properties, but these are much less marked than in the corresponding bromine compound; the negative influence of the dinitrophenyl therefore has been partly neutralised by the introduction of the basic aniline radical C_6H_5NH.

The Sodium Salt, $C_6H_2(C_6H_5NH)(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was formed in the same way as the sodium salt of the bromdinitrophenylmalonic ester; that is, by treating an alcoholic solution of the substance with alcoholic sodic hydrate not in excess, evaporating to dryness with a little ether on the water-bath, and extracting the excess of the ester with benzol. It was dried at 100°, and analysed.

0.1180 gram of substance gave 0.0194 gram of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.
Sodium,	5.24	5.32

Properties.—It resembles the sodium salt of the bromdinitrophenylmalonic ester closely in appearance and solubility, but is of a somewhat lighter red. Its solution is decomposed when treated with carbonic dioxide.

Experiments on the Saponification of Bromdinitrophenylmalonic Ester.

In taking up this subject we considered it necessary to study the action of alkalies on the ester, although, owing to the ease with which the nitro groups are attacked, we had little expectation of reaching satisfactory results. In this we were not deceived, but we think it best to give a brief account of these experiments before describing our more successful work with strong hydrochloric acid in sealed tubes.

A solution of sodic hydrate in water, if boiled with the brom- or anilidodinitromalonic ester, gave a brownish red solution, from which acids precipitated nothing; but after acidification, and extraction with ether, an unpromising oil was obtained in very small quantity. Cold alcoholic sodic hydrate with the anilido compound gave a somewhat more promising result, but in this case also most of the substance seemed to be decomposed. The bromine compound, after standing for two weeks with ammonic hydrate at ordinary temperatures, was converted into a similar brown solution, which on acidification gave a resinous brown precipitate and a yellow filtrate, from which ether extracted a substance melting above 200°, ammonic bromide being formed during the process. This is the only one of these products which seems worth further investigation.

Action of Hydrochloric Acid.[1]

When the bromdinitrophenylmalonic ester was heated with strong hydrochloric acid in a sealed tube to 140°–145°, it was decomposed, and upon opening the tube a gas was given off in tolerable quantity, which burnt with a green-bordered flame, and was without doubt ethyl chloride. About one gram of the substance and 20 cc. of common strong hydrochloric acid were used in each tube, and the temperature should not be allowed to go above 150°, as in this case an impure product was the result. If proper care was used in the heating, the tube contained crystals, or a clear liquid from which crystals were deposited after the pressure was relieved; these were filtered out and the filtrate thrown away, as it gave almost no residue on evaporation, and no extract when shaken with ether.

The crystals were purified by crystallisation from dilute alcohol (three parts of water to one part of alcohol). If the temperature was kept below 150°, the product was nearly pure, as it came from the tube; but if it had risen above this point, a small quantity of a lower melting substance was formed, which it was almost impossible to remove with dilute alcohol. In this case the best plan was to dissolve the substance in chloroform, when the impurity separated at first as a pasty mass, leaving the principal product in solution, which after one crystallisation from dilute alcohol showed the constant melting point 170°.[2]

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[1] All our work on this part of the subject must be regarded as preliminary.

[2] Later work has shown that it is essentially impossible to purify the substance by crystallisation from dilute alcohol, and that when pure it melts at 177°, not at 170°. We have withdrawn, therefore, from this paper the analyses made last year of the substance melting at 170°, and prefer to make no statement about the composition of the substance, until the investigation of it, upon which we are now engaged, has come to a conclusion.

Properties.—The substance crystallises from dilute alcohol in yellowish white narrow plates, sometimes half a centimeter in length, which are made up of needles attached to another needle acting as a midrib at very acute angles, giving an exact imitation of a feather, or more commonly of one side of a feather; this form is very characteristic, and, when not so well developed, the substance can be recognised by the formation of narrow plates, usually smooth on one side and rather irregularly serrated on the other or upon the ends. The plates often occur in radiating groups, the members of which form very acute angles with each other. From methyl alcohol or ether it crystallises in very slender needles, much branched at very sharp angles, often forming circular groups resembling certain seaweeds. It melts at 170°, is not very soluble in cold alcohol, freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in glacial acetic acid or acetone, tolerably soluble in ether, slightly soluble in benzol either cold or hot, or in carbonic disulphide; slightly soluble in cold chloroform, more soluble but not freely in hot, nearly insoluble but not quite so in cold water, more soluble but still very slightly in hot, essentially insoluble in ligroine. The best solvent for it is chloroform, or a mixture of alcohol and water. Its behavior with alkalies is very characteristic. If a drop of an aqueous solution of sodic hydrate is added to the substance dissolved in alcohol, the solution takes on a dark but brilliant Prussian green color. This solution becomes colorless on addition of hydrochloric acid, but turns green again on addition of sodic hydrate. The green alcoholic solution, if allowed to evaporate spontaneously, leaves a brownish yellow residue, and a solution of the same brownish yellow color is obtained if an *excess* of sodic hydrate is added to the original substance. If the yellow solution, in whichever way prepared, is acidified with hydrochloric acid, it loses its color, and oil-drops are precipitated, which solidify in time. These dissolve in sodic hydrate with a brownish claret[1] or pale magenta color, which is unaltered by dilution with water, but turns green on addition of alcohol. The substance melting at 170° is not affected by an aqueous solution of sodic carbonate. The further study of these interesting reactions has been broken off by the summer vacation, but will be continued in this laboratory in the autumn.

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[1] A somewhat similar change of color was observed during the action of ethylbromide on the sodium salt of the bromdinitrophenylmalonic ester.

THE RATES OF TRANSFERENCE AND THE CONDUCTING POWER OF CERTAIN SILVER SALTS.[1]

BY WALTHER NERNST AND MORRIS LOEB.

1. *Introduction.*

Whenever a current of electricity is passed through a conductor of the second class, under such conditions that the composition of the solution is not changed, as when a current passes between electrodes of the same metal in a solution of a salt of that metal, curious changes of concentration appear. This was noticed by many scientists, but it was reserved for Hittorf to investigate these changes quantitatively and to advance a plausible and exhaustive hypothesis of their causes. His work constitutes one of the classics in physics; but as it is not, perhaps, so generally known to chemists, a short explanation of his hypothesis may be a not inappropriate introduction to our paper. Taking the example already cited, it is, of course, a familiar principle, that in a given interval the same amount of metal is dissolved from the positive electrode as is deposited upon the negative electrode. If we were to assume that the ions of the electrolyte were incapable of moving independently of each other, the changes in concentration at the two electrodes could only be counterbalanced by the slow process of diffusion, and we should find a deficit in the liquid around the negative electrode corresponding to the amount of metal deposited upon the latter, while all the metal yielded up by the positive electrode would be found in its immediate surroundings. This is, of course, an untenable assumption. Supposing, on the other hand, that only the negative ions were immovable, while the positive ones could travel across the liquid as fast as required to supply the places of those disappearing upon the negative electrode: the liquid would be homogeneous at all moments, and there would be no concentration nor dilution around the electrodes. We cannot, however, assume that the negative ions are immovable, everything showing that they move toward the cathode just as well as the positive ones do toward the anode. If both move with equal rapidity, as was tacitly assumed before Hittorf, a little reflection will show that the liquid about the cathode will lose just half as much metal as is deposited upon the electrode, while half the metal given up by the anode to the surrounding liquid will have been transferred toward the cathode. Hittorf's laborious analyses proved that none of these three possibilities was fulfilled. The relation between the changes in concentration and the amount of metal transferred from one electrode to the other proved conclusively that the two classes of ions did not move with equal rapidity; and he showed how this ratio provided a measurement of the share of each class in the total movement. For any salt, the ratio of the weight of the metal deposited to the amount of metal lost by the fluid around the cathode (or its equivalent, the amount gained by that around the anode) represents the share of the negative ion, the anion, in the total movement.

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[1] Abbreviated translation from the paper appearing in the Zeitschrift für physikalische Chemie **2**, 948, made for this Journal by one of the authors.

Hittorf has had few followers in these investigations,[1] as the difficulties of experiment were discouraging. Analytical accuracy demanded the use of concentrated solutions, or of bulky and cumbrous apparatus, while it was especially desirable to study dilute solutions, and to use apparatus which was not subject to such disturbances as variations of temperature, osmose, and the jars unavoidable during mechanical handling produce. Considerations which will be explained later led us to attempt the acquisition of fresh material, especially with reference to highly dilute solutions. We found that we could do this by studying certain silver salts, mainly organic; and we were led to this choice firstly because silver is the only monovalent metal which furnishes a satisfactory electrode—a matter of some moment for our subsequent work; secondly, because its salts are readily obtained in the needful state of purity; finally, because Volhard's beautiful method of titration[2] enabled us to perform the necessary analyses with great ease and extreme nicety. We also availed ourselves of the opportunity for studying the effects of temperature and concentration upon the velocity of the ions of these salts, because one of us[3] has recently shown how important a part is played by these factors in the kinetics of solutions.

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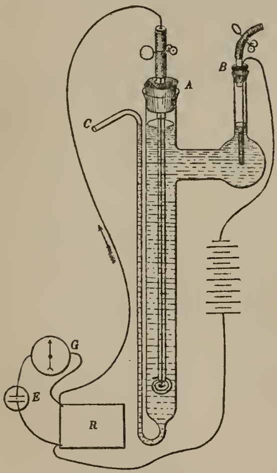
[1] The following list includes all the literature: Hittorf, Ann. der Phys. Pogg. **89**, 177, **98**, 1, **103**, 1, **106**, 337; G. Wiedemann, ibid. **99**, 177; Weiske, ibid. **103**, 466; Kuschel, Ann. der Phys. Wied. **13**, 289; Kirmis, ibid. **4**, 503; Lenz, Mém. Ac. Petersbourg **30**, 1882.

[2] Volhard, Ann. Chem. (Liebig) **190**, 1.

[3] Nernst, Zeitschrift für physikalische Chemie **2**, 613.

2. *Apparatus for the Determination of the Rate of Transference.*

In this apparatus we wished to avoid the use of membranous diaphragms, and to minimise the internal resistance, necessarily large by reason of our very dilute solutions, so as to keep the necessary duration of an experiment within reasonable limits. After various failures we finally hit upon a form whose simplicity is likely to recommend it in similar cases. As shown in the accompanying drawing, it is seen to resemble the Gay-Lussac burette, but with the addition of a short side-tube of the same bore as the main tube. This side-tube ends in a bulb, and upon this is set a narrower vertical tube, through which the negative electrode—a cylindrical roll of silver foil fastened to a silver wire—can be let down into the bulb. This works as a sort of pocket, by which masses of the spongy precipitated silver that may become detached from the electrode are prevented from stirring up the body of the solution. The anode consists of a silver wire rolled into a spiral at the lower end. It is introduced through *A*, and reaches to the bottom of the main tube. In order that the current may enter the liquid only at the spiral, the straight part of the wire is covered with a capillary of very thin glass, which can be closed around the wire by fusion, in spite of the difference in their coefficients of expansion. The openings *A* and *B* are closed with corks that are traversed by short glass tubes. Of these, the tube at *A* allows free passage to the wire of the electrode. The wall of the tube at *B* is pierced by a platinum wire, which serves to suspend the cathode and to connect it with the conductor of the battery. Thus *A* can be closed by the compression of a bit of rubber tubing drawn over the wire and glass tube, or air can be sucked or blown through a rubber tube connected with *B*, without disturbing the electrodes.



In experimenting, such an apparatus would first be weighed with its electrodes and stoppers, but without the rubber tubing. The latter was hereupon put in position, *A* was closed with a pinch-cock as just indicated, and air was drawn out at *B* while the nozzle *C* was dipping under the surface of the solution to be used. By this process, the main- and side-tubes were filled up to the level of the top of the latter; the sizes of apparatus we employed contained 40 and 60 cc. respectively. The nozzle was now likewise closed with a rubber cap, and the whole apparatus suspended in such a fashion, in one of Prof. Ostwald's thermostatic water-baths,[1] that the nozzle protruded over the rim, while the liquid was entirely within the water-bath. After it had acquired the temperature of the bath, the circuit was closed. As soon as the electrolysis was concluded, the nozzle was opened and suitable portions of the liquid were filled into tared vessels, by blowing steadily through *B*. These portions were weighed and analysed. The portion remaining in the apparatus was estimated by the latter's gain in weight, and likewise analysed. Provided there has been no mixing through diffusion and convection during the electrolysis, the first portion taken from the apparatus, if the liquid is properly divided, will consist of the stratum around the anode, which has become more concentrated, and of a sufficient quantity of the unaltered middle layers to insure a rinsing of the adhering parts of the lowest stratum. The succeeding portions being composed wholly of the middle layers, must show an unaltered composition, while what is left in the apparatus includes the diluter strata about the cathode. To prove the reliability of our experiment, we must find in the first place that the middle layers had remained unchanged, and secondly, that the gain of the lowest layer exactly counterbalanced the loss of the highest, for the mean composition of the whole liquid undergoes no change. After finding that the first condition was invariably fulfilled, we saved time by giving up the separate examination of the middle layers, and divided the whole liquid into two nearly equal portions. It frequently happened that, during the electrolysis, the electrolysed silver would grow out from the bulb along the wall of the horizontal tube. In such cases the circuit was broken before the silver had reached the main tube; otherwise, we disconnected whenever we estimated that a sufficient change of concentration had taken place to give the most reliable results.

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[1] As described recently by Prof. Ostwald, Ztschr. phys. Chem. 2, 565.

The analyses were performed, as already intimated, by titration with a solution of ammonic sulphocyanate, the standard of which (about $\frac{1}{100}$ normal) was ascertained by frequent comparison with an argentic nitrate solution of known strength, occasional gravimetric determinations of which gave absolutely constant results. We claim for the titrations an error well within $\frac{1}{30}$ cc. ($= 0.038$ milligrams Ag), each end-reaction being observed twice, as 1 cc. of a $\frac{1}{100}$ normal solution of argentic nitrate was added from a pipette, after the first appearance of the characteristic tint, and the titration repeated.

The ratio we are seeking to determine requires, besides the data of the change in concentration, the weight of the silver which has been actually deposited upon the cathode, in the same interval of time. This would most naturally be determined by a silver voltameter placed in the same circuit with the apparatus. But as the examination of dilute solutions often necessitated the deposit of less than 20 milligrams in all, and the silver is deposited in such a form upon the voltameter that it is difficult to weigh it without a slight loss, we found it to be more advantageous to determine the quantity of electricity which traversed the apparatus by galvanometric measurement. A resistance-box was introduced into the circuit for this purpose (see figure), to the extremities of which a second circuit was connected, containing a Clark's cell and a galvanometer with direct reading. The Clark's cell being introduced in the proper direction, it is well known that a suitable resistance R may be introduced by means of the box, which will put the galvanometer at rest at the O point; when this is effected, we have for the electrical intensity of the main current $i = \frac{E}{R}$, E denoting the electromotive force of the standard Clark's cell. As the intensity of the current changed but little and very gradually during the four or five hours which were usually occupied by an electrolysis, we were satisfied with making this measurement, which required but a few seconds' attention, every ten minutes. The total amount of electricity could then be integrated with sufficient certainty.

Special experiments showed that, when resistance-box and

Clark's cell were at a temperature of 18° C., the quantity f of precipitated silver could be found by the formula,

$$f = \frac{\tau}{r} 92.69,$$

where τ represents the duration of the electrolysis in minutes, while r denotes the resistance which would have been necessary to keep the galvanometer at *O*, provided that amount of electricity which actually passed through the apparatus had done so in a current which remained constant throughout this interval. Whenever the resistance-box and the cell were at any other temperature, t, the above expression must be multiplied with the factor $1 - 0.0012(t - 18)$. This coefficient of temperature, 0.0012 is derived from that of the cell, -0.0008, and that of the box, $+0.0004$.

Our battery consisted of 38 Leclanché cells, with a combined electromotive force of about 40 volts and an internal resistance of about 120 ohms. It furnished a current which remained practically constant for many hours, when enclosed in a circuit of 5000—10,000 ohms resistance. It also had the advantage of being always ready for use.

3. *Preparation of the Silver Solutions.*

The solutions of argentic nitrate were prepared from the crystallised salt. Those of the chlorate, perchlorate, ethyl-sulphonate, naphthalene-sulphonate, benzene-sulphonate, pseudo-cumene-sulphonate and acetate, were made by neutralising known amounts of these acids with moist argentic oxide, passing the solution through an asbestos filter, and diluting to a suitable volume. Argentic dithionate ($Ag_2S_2O_6$) was obtained by the reaction of exactly equivalent quantities of baric dithionate and argentic sulphate. To make argentic fluosilicate, a solution of hydrofluosilicic acid was saturated with argentic oxide; dilute baric hydrate solution was then added cautiously, until the brown color of argentic oxide commenced to appear in the precipitate of baric fluosilicate. The neutral solution was then filtered and diluted.

4. *Description of a Determination in Detail.*

The description of this determination, made with a solution of argentic nitrate which was about $\frac{1}{10}$ normal, will best illustrate our method of experiment and calculation. The electrolysis was conducted at a temperature of 26°, and the solution thereupon divided into four portions, which are numbered in the following table in the order in which they were taken out; consequently, No. 1 represents the *lowest* stratum in the apparatus. Column I contains the weights of these portions; II, the amount of silver found in each; III, the amount each portion would have contained if no change had occurred, estimated from the fact that 1 gram of the solution originally contained 1.139 milligram of silver.

TABLE I.

Portion.	I.	II.	III.	Diff.
1	20.09 grams	39.66 millig.	22.88 millig.	+ 16.78 millig.
2	5.27	5.96	6.00	— 0.04
3	5.33	6.04	6.07	— 0.03
4	27.12	14.14	30.89	— 16.75
	57.81	65.80		

It will be seen that the strength of two middle portions has remained constant, within the errors of determination; we also find a close agreement in the second test, which demands that the mean concentration shall remain unchanged; the value 65.80/57.81 = 1.138, scarcely different from the original strength 1.139.

The measurement of the electrical current as described above informed us that a quantity of electricity equivalent to the precipitation of 32.10 mg. of silver had passed through the apparatus; while a silver-voltameter, placed in the circuit for our better assurance, contained 32.2 mg.; the former value was accepted as the more trustworthy.

Following Hittorf,[1] we based these calculations upon our data: The solution at the anode (1) received from the latter 32.1 mg. Ag, and the uppermost layer (4) gave up the same amount to the cathode. Owing to the changes in concentration, the values in the above table are not absolutely correct, since 1 gram of solution does not always contain the same weight of water, as had been provisionally assumed. But the necessary correction is small and readily made. Let ν be the ratio of the molecular weights of silver and the salt in question; in this special case $\nu = \frac{170}{108} = 1.57$. Let a represent the amount of silver contained in 1 gram of unaltered solution, being consequently dissolved in $(1 - a\nu)$ grams of water. If, after electrolysis, q grams of the solution about one electrode are found to contain b grams of silver, the gain or loss will be represented by $\pm b - \frac{a(q - b\nu)}{1 - a\nu} = \pm \frac{b - aq}{1 - a\nu}$. As $b - aq$ is the value given in the column of differences, the factor $\frac{1}{1 - a\nu}$ represents the necessary correction. Consequently, after completing the deficit of portion 4 by the addition of the small deficits in 2 and 3, we have for the *rate of transference of the negative ion*,

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[1] Hittorf, Ann. Phys. Pogg. **98**, 19.

$$\frac{16.78}{32.10} / .0017 \text{ and } \frac{16.82}{32.10} / .0017, \text{ or a mean value of } 0.524.$$

As already stated, the determination was usually simplified by dividing the liquid into two portions instead of four.

In this experiment there was a second apparatus placed in series in the circuit; hence the mean intensity of the current was only 0.0012 ampère, and the electrolysis lasted seven hours. We frequently saved time and used our battery to better advantage by performing two simultaneous electrolyses in parallel circuits, each of which must, of course, contain its own resistance-box; by means of a properly constructed switch, we could apply the measuring circuit to either box at will, thus securing the measurement of both electrolyses with the same galvanometer and element. We may also state here that the last was frequently compared with another cell of the same construction and was always found to be exactly equivalent to it in electro-motive force, a proof that it did not vary during the course of our experiments.

5. *Rates of Transference of the Negative Ion.*

Hereafter t implies the temperature during electrolysis; m the molecular concentration (gram-molecules per liter); f_1 the milligrams of silver precipitated on the cathode according to galvanometric measurement; f_2 the same value according to the voltameter whenever it was used; n the rate of transference.

Argentic Nitrate.

1)	$t = 20°$	$m = 0.1043$	$f_1 = 83.5$	$f_2 = 83.6$	$n = 0.528$
2)	$t = 26°$	$m = 0.0521$	$f_1 = 76.7$		$n = 0.524$
3)	$t = 26°$	$m = 0.0250$	$f_1 = 48.0$		$n = 0.5223$
4)	$t = 0°$	$m = 0.0250$	$f_1 = 48.0$		$n = 0.5383$
5)	$t = 26°$	$m = 0.0105$	$f_1 = 32.10$	$f_2 = 32.2$	$n = 0.524$
6)	$t = 26°$	$m = 0.0105$	$f_1 = 32.10$	$f_2 = 32.2$	$n = 0.524$

In 3) and 4) and in 5) and 6) both pieces of apparatus were in the same circuit.

Argentic Chlorate.

1) $t=24.8^\circ$ $m=0.0245$ $f_1=39.88$ $f_2=39.5$ $n=0.503$
2) $t=24.8^\circ$ $m=0.0245$ $f_1=51.72$ $n=0.499$

Argentic Perchlorate.

1) $t=24.8^\circ$ $m=0.0247$ $f_1=39.88$ $f_2=39.5$ $n=0.515$
2) $t=24.8^\circ$ $m=0.0247$ $f_1=51.72$ $n=0.512$

In studying these two solutions, 1) and 1) and 2) and 2) were in the same circuits.

Argentic Ethyl-sulphonate.

1) $t=24.8^\circ$ $m=0.0243$ $f_1=58.30$ $n=0.385$
2) $t=24.8^\circ$ $m=0.0243$ $f_1=48.47$ $f_2=48.34$ $n=0.389$
3) $t=25^\circ$ $m=0.00606$ $f_1=18.10$ $n=0.384$

Argentic Benzene-sulphonate.

1) $t=24.8^\circ$ $m=0.0250$ $f_1=48.47$ $f_2=48.34$ $n=0.343$
2) $t=24.7^\circ$ $m=0.0250$ $f_1=17.85$ $n=0.351$

2) of the former and 1) of the latter solution were electrolysed in series.

Argentic Pseudocumene-sulphonate.

1) $t=24.2^\circ$ $m=0.0235$ $f_1=61.62$ $n=0.293$
2) $t=29.2^\circ$ $m=0.02216$ $f_1=38.24$ $n=0.2947$
3) $t=0^\circ$ $m=0.02216$ $f_1=38.24$ $n=0.2732$
4) $t=0^\circ$ $m=0.02216$ $f_1=42.79$ $n=0.2731$

2) and 3) were electrolysed in series.

Argentic Naphthalene-sulphonate.

1) $t=29.2^\circ$ $m=0.01292$ $f_1=33.95$ $n=0.390$
2) $t=25.0^\circ$ $m=0.0250$ $f_1=39.75$ $f_2=39.5$ $n=0.386$

Argentic Acetate.

In examining this salt, we were surprised to find that the middle layers of the solution did not remain unchanged, and that the mean concentration after electrolysis did not agree with the original standard. This irregularity is probably due to the slight solubility of the salt, since it can easily happen that the solution about the anode becoming over-concentrated, some of the salt crystallises out and vitiates the result. In fact, we did succeed in obtaining reliable values when we had recourse to a highly dilute solution.

1) $t = 25°$ $m = 0.00972$ $f_1 = 20.80$ $n = 0.375$
2) $t = 24°$ $m = 0.0c972$ $f_1 = 23.99$ $n = 0.377$

Argentic Dithionate.

1) $t = 24.8°$ $m = 0.0246$ $f_1 = 33.40$ $n = 0.604$
2) $t = 29.2°$ $m = 0.0246$ $f_1 = 46.70$ $n = 0.604$
3) $t = 0°$ $m = 0.0246$ $f_1 = 46.70$ $n = 0.605$
4) $t = 24.2°$ $m = 0.0246$ $f_1 = 48.85$ $n = 0.606$
5) $t = 0°$ $m = 0.0246$ $f_1 = 45.80$ $n = 0.603$

2) and 3) were electrolysed in series.

Argentic Fluosilicate.

1) $t = 22.2°$ $m = 0.02815$ $f_1 = 60.28$ $n = 0.647$
2) $t = 22.2°$ $m = 0.02815$ $f_1 = 37.44$ $n = 0.647$

In table II we summarise these values of n, with the corresponding temperatures and concentrations.

TABLE II.

Argentic	*n.*	*t.*	*m.*
Nitrate, ...	0.523	25°	0.1 — 0.01
	0.539	0°	
Chlorate, ...	0.505	25°	0.0245
Perchlorate, ...	0.514	25°	0.0247
Ethylsulphonate, . . .	0.385	25°	0.0243 — 0.0061
Naphthalene-sulphonate, .	0.390	30°	0.0250 — 0.013
	0.386	25°	
Pseudocumene-sulphonate,	0.293	25°	0.023
	0.273	0°	
Benzene-sulphonate, . .	0.347	25°	0.025
Acetate, ...	0.376	25°	0.097
Dithionate, ...	0.604	25°	0.0246
	0.604	0°	
Fluosilicate, ...	0.466	22°	0.0282

Argentic nitrate has been carefully studied by Hittorf,[1] who found that between the concentrations 0.3 and 0.024 the rate of transference does not vary, the mean value being 0.526 at 19°. We came to the same conclusions for variations of concentration from 0.1 to 0.01, and we found a value which, when reduced to the same temperature, very nearly agreed with his, 0.527 at 19°. The acetate result given above also agrees well with Hittorf's (0.373 where $t = 15°$ and $m = 0.05$).

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[1] Ann. Phys. Pogg. **89**, 199.

6. *Conducting Power of the Silver Salts and its Relation to the Rate of Transference.*

It will be noted that the rate of transference is a value varying with the compound, since it merely expresses the share of the one ion in the total movement. If u is the actual velocity of the positive ion and v that of the anion, $n = \frac{v}{u + v}$; and the rate of the positive ion, $1 - n = \frac{u}{u + v}$. Kohlrausch,[1] as is well known, has propounded the simple hypothesis that the conducting power of a molecule of an electrolyte is represented by the sum of the velocities of its ions,

$$\lambda = u + v.$$

His experiments, however, did not seem to give the requisite support to this theory, some salts giving approximate results, but those of weak bases and acids giving utterly discordant figures. The difficulty is removed if we assume that the conduction is not performed by all the molecules of the electrolyte, but only by those whose ions are actually in independent motion. This is Arrhenius' principle of conductive activity.[2] Kohlrausch's values for molecular conductivity are a function of the total number of molecules of the electrolyte between the electrodes; according to Arrhenius, the coefficient of activity, *i. e.* the proportion of molecules actually engaged in conduction, not only varies for different compounds, but also increases for any one compound with its dilution, and approaches unity for extreme dilutions. It is only in this limiting case that Kohlrausch's equation becomes absolutely true; this is the view that Kohlrausch himself had expressed with regard to his law, whose accuracy, he said, could only be tested by experiments with highly dilute solutions. Ostwald's examination of the conducting power of highly attenuated solutions of a very large number of electrolytes[3] has afforded very valuable support to these recent views.

Since, however, the quantities u and v are so closely connected with the rate of transference of the ions, a study of the latter in dilute solutions must afford powerful means of testing the truth of Kohlrausch's law with Arrhenius' emendations. This was the chief motive of our work, and we must now, therefore, proceed to compare the values which we have given in §5 with the conducting power of the same salts. Accordingly, the necessary measurements of conduction were made by one of us (W. N.), by Kohlrausch's method, which with various valuable modifications has been described by Prof. Ostwald.[1] The values which we present are scaled upon the conducting power of mercury as unity, and the calculations are based upon Kohlrausch's determination of the molecular conductivity of argentic nitrate.[2]

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[1] Fr. Kohlrausch, Ann. Phys. Wied. **6**, 1.

[2] S. Arrhenius, Sur la conductibilité, etc., Stockholm, 1884.

[3] Ztschr. phys. Chem. **1**, 61 and 97.

The following table gives the conducting power of the different silver salts. The molecular concentration (gram-molecules in the liter) *m*, was calculated from the percentage composition as found by analysis, and the specific gravity determined at 18°, although this barely differed from that of water. There was no appreciable contraction when additional water was added for dilution; but a proper correction was made for the conduction by the water itself, which was found to be 2.5×10^{-10}.

TABLE III.

m.	$\lambda \times 10^8$ at 25°.				
	$AgNO_3$.	$AgClO_3$.	$AgClO_4$.	$Ag(C_2H_5SO_4)$.	$Ag(C_6H_5SO_3)$.
0.025	1126	1045	1109	...	...
0.015	1153	1103	1139	...	846
0.007	1188	1123	1160	905	874
0.003	1206	1151	1182	930	897
0.0015	1221	1160	1194	943	900
0.0008	1232	1163	1200	949	906

m.	$\lambda \times 10^8$ at 25°.				
	$Ag(C_9H_{11}SO_3)$.	$Ag(C_{10}H_7SO_3)$.	$AgC_2H_3O_2$.	$\frac{1}{2}Ag_2S_2O_6$.	$\frac{1}{2}Ag_2SiFl_6$.
0.025	734	...	...	1253	995
0.015	762	882	...	1343	1020
0.007	791	893	897	1383	1054
0.003	813	926	926	1442	1081
0.0015	826	941	944	1474	1096
0.0008	836	951	949	1505	1100

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[1] Ibid. 2, 563.

[2] As Kohlrausch worked at 18°, while the present determinations were made at 25°, the coefficients of temperature were determined by special experiments for various dilutions of $AgNO_3$. For the details of these results we must refer to the German version of our paper.

Ostwald has found[1] that the sodium salts of numerous monobasic acids have almost identically progressing coefficients of activity; the same regularity may be observed in the present series. The ratios of the conductivity of a salt in various states of dilution agree, for the silver salts of the monobasic acids, within limits that scarcely transcend the probable errors of observation. We shall utilise this fact in finding the limit of the conductivity for extreme dilution; for, at the concentration 0.0008, the dissociation of the molecules is not yet complete, although very nearly so. If we remember that, according to Kohlrausch's measurements, when $m = 0.0008$, $\frac{1069}{1077}$ of the molecules of argentic nitrate are dissociated, we can fairly assume that the limiting values of λ for the other silver salts may be obtained by raising by 0.75 per cent. the values found for $m = 0.0008$.

Table IV summarises the measurements made to determine the effect of temperature upon conducting power; in these the platinum electrodes usually employed were replaced by silver ones, which gave very sharp readings. The measured conductivities at 0°, 18° and 28° are denoted by λ_0, λ_{18} and λ_{28} respectively; to obtain the coefficient of temperature $\frac{\lambda_{28}}{\lambda_{18}}$ must be diminished by 1 and divided by 10: $\frac{\lambda_0}{\lambda_{25}}$ was calculated from such an interpolated value of λ_{25}.

TABLE IV.

	m.	$\frac{\lambda_0}{\lambda_{18}}$	$\frac{\lambda_{28}}{\lambda_{18}}$	$\frac{\lambda_0}{\lambda_{25}}$
$AgNO_3$, ...	0.1	0.638	1.213	0.555
	0.02	0.638	1.217	0.554
	0.005	0.632	1.222	0.548
$AgClO_3$, ...	0.005	0.626	1.222	0.542
$AgClO_4$, ...	0.005	0.632	1.224	0.547
$AgC_{10}H_7SO_3$, . .	0.005	0.615	1.242	0.526
$AgC_6H_5SO_3$, . . .	0.005	0.607	1.241	0.519
$AgC_2H_3O_2$, . . .	0.005	0.611	1.237	0.524
$AgC_9H_{11}SO_3$, . .	0.025	0.609	1.242	0.521
	0.006	0.606	1.246	0.517
$\frac{1}{2}Ag_2S_2O_6$, . . .	0.025	0.631	1.222	0.547
	0.006	0.631	1.226	0.544

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[1] Ostwald, Ztschr. phys. Chem. **2**, 847.

7. *Test of the Law of Kohlrausch for Extreme Dilutions.*

For this purpose we need, besides the limiting values for conduction, which we have just shown to be attainable, the limiting values for the rate of transference, likewise for extreme dilution.

At the close of section 5 we noted that Hittorf found the value of n to be independent of the state of dilution where $m < 0.3$ in the case of $AgNO_3$, and that we confirmed his result by our own experiments on this and other salts. Consequently the values found for this rate, whenever $m = 0.025 - 0.01$, can be assumed to hold good for infinite dilutions. The reason becomes apparent when, considering the inactive molecules as stationary, we remember that a molecular concentration 0.01 means a proportion of one silver ion to 5550 molecules of H_2O. The resistance which such an ion would encounter cannot differ from that of pure water.

The testing of Kohlrausch's law can now be readily accomplished by multiplying the limiting value of conductivity into $(1 - n)$, the rate of transference of the positive ion; the product, which represents the molecular velocity of the silver ion, must remain constant for all the monobasic salts.

TABLE V.

	$\lambda \times 10^8$.	$(1 - n)$.	$\lambda (1 - n) 10^8$.
$AgNO_3$,	1242	0.477	592
$AgClO_3$,	1172	0.499	585
$AgClO_4$,	1208	0.486	587
$AgC_2H_5SO_4$,	956	0.615	588
$AgC_{10}H_7SO_3$,	958	0.614	588
$AgC_6H_5SO_3$,	913	0.653	596
$AgC_9H_{11}SO_3$,	842	0.707	595
$AgC_2H_3O_2$,	956	0.624	597

The velocity of Ag as found in these salts proves to be nearly constant: the deviations from the average 591×10^{-8} are within the limits of the probable errors of observation, especially as the latter have a cumulative effect. We consider this an additional confirmation of the recent electrolytic hypotheses.

This average, which applies for 25°, may be considered the true value for the velocity of the Ag ion, within a few thousandths, provided Kohlrausch's determination of the limit of conduction for argentic nitrate contains no important error. We can now calculate the ion's velocity at 0°, from the values of n at that temperature for argentic nitrate and pseudo-cumol-sulphonate (table II), and the values of λ reduced from table III by the ratio $\frac{\lambda_0}{\lambda_{25}}$ (table IV).

$$1242 \times 0.461 \times 0.548 = 314$$
$$842 \times 0.727 \times 0.517 = 317 \quad \text{Mean} = 315.5.$$

We again call attention to the smallness of the deviation. Now, since $\lambda = u + v$, we can obtain the velocities of all our negative ions, by subtracting the velocity of the silver from the respective conducting powers. In table VI we find on the first line the velocities at 25°; on the second, those at 0°; on the third, the coefficient of temperature between 25° and 0°, as calculated from the formula $v = v_{25}\,[1 + \alpha\,(t - 25)]$, α being the coefficient: all the values must be multiplied by the factor given in the final column.

TABLE VI.

	$C_9H_{11}SO_3$.	$C_6H_5SO_3$.	$C_2H_3O_2$.	$C_2H_5SO_4$.	
I	248	318	361	368	$\times 10^{-8}$
II	118	156	183	...	$\times 10^{-8}$
III	210	203	197	...	$\times 10^{-4}$

	$C_{10}H_7SO_3$.	ClO_3.	Ag.	ClO_4.	NO_3.	
I	369	587	591	621	640	$\times 10^{-8}$
II	180	322	316	347	364	$\times 10^{-8}$
III	198	181	186	177	175	$\times 10^{-4}$

The close agreement of the velocities shown in line I with the observations of the rates of transfer and of the conduction, is proved by the fact that the calculated and observed values agree within ½ per cent. in all cases. A glance at table VI, in which the velocities are arranged according to magnitude, will bring out a striking relation of the coefficients of temperature. *The coefficient of temperature decreases when the velocity increases.* We may add that the coefficients of temperature for the monovalent ions OH and H, which have an exceptionally great velocity, can be added to this series.[1]

	OH.	H.	
I	187	350	$\times 10^{-7}$
III	159	137	$\times 10^{-4}$

A result of this regularity would be that, as the temperature rises, the rates of transference would all approach the value 0.5, and the conducting powers λ_∞ of all salts would approach equality.[2]

If we attempt to calculate the velocity of the silver ion from the salts of the two dibasic acids which we have studied, we obtain from

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[1] Nernst, Ztschr. phys. Chem. **2**, 626.

[2] Cf. Arrhenius, l. c. p. 45.

$$Ag_2S_2O_6: 1540 \times 0.394 = 0.607$$
$$Ag_2SiF_6: 1120 \times 0.534 = 0.598$$

These values are somewhat greater than those found before. To avoid a conflict with the necessary assumption that the free ion of silver must have the same velocity, no matter whether it has been liberated from a mono- or dibasic acid ion, we must admit that the rates of transfer in these two salts, which were measured at a concentration 0.025 and 0.028 respectively, must change on further dilution. As our investigation was brought to a close by the departure of one of us from Leipsic, we were unable to set this question at rest; we note in passing, however, that the dissociation hypothesis makes it probable that the compounds of multivalent radicals are still undergoing changes at dilutions in which monobasic compounds show a constant rate of transference. The dissociation products for $Ag_2S_2O_6$, for instance, are Ag, AgS_2O_6 and S_2O_6; consequently in such dilutions as 0.025 there may exist, besides the ions $+ Ag$, $+ Ag$, $- S_2O_6$, upon which we based our calculations, a considerable set of ions $+ Ag$, $- AgS_2O_6$; if these decompose on further dilution, the rate of transference must continue to change. We have here considerations similar to those which Hittorf used so skilfully nearly thirty years ago,[1] in obviating the difficulties which the abnormal behavior of cadmic iodide threatened to cast in the way of his theory.

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DECOMPOSITION OF COBALT AND NICKEL.[2]

BY GERHARD KRÜSS AND F. W. SCHMIDT.

We have been engaged in a redetermination of the atomic weights of cobalt and nickel, employing the method first devised by Clemens Winkler, of decomposing gold chloride solution by weighed amounts of cobalt or of nickel, and weighing the precipitated gold, thus obtaining the equivalents of cobalt or nickel in terms of gold. As Krüss recently redetermined with great accuracy the atomic weight of gold, this method promised better results than when it was first employed by Winkler twenty years ago, and we hoped to confirm in this way the figures found by Clemens Zimmermann in his determination—cobalt 58.74, nickel 58.56.

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[1] Hittorf, Ann. Phys. Pogg. **106**, 546 (1859).

[2] Abstract of an article in Ber. d. chem. Ges. **22**, 11; prepared by E. Renouf.

Despite numerous attempts, we neither succeeded in obtaining Zimmermann's figures, nor in confirming the atomic weights formerly found by Winkler by the same method. We first found that it is impossible to precipitate quantitatively by nickel or cobalt from a neutral gold chloride solution an equivalent amount of gold, because in consequence of polarisation the precipitated gold attacks the nickel or cobalt chloride solution which has been formed, reversing the original reaction and reprecipitating minute quantities of cobalt or nickel which remain undissolved mixed with the gold. To determine how much metal had taken part in this secondary reaction, the precipitated gold was washed, dried, ignited, and weighed, then dissolved in *aqua regia*, and after evaporating all free acid, reprecipitated by sulphurous acid, and weighed. There was a noticeable loss of weight between the two weighings, and the difference was deducted from the weight of the metallic nickel or cobalt first taken.

Despite these precautions, such varying figures were obtained that the variations were evidently due to some other cause than ordinary analytical errors. In washing the gold which had been reprecipitated by sulphurous acid, the filtrate had a red color, due to cobalt chloride. We noticed that the wash-water dripping from the filter gradually lost this red color and became tinged with a greenish hue, so slight that it had before escaped observation. This part of the wash-water was evaporated in a platinum dish and left a slight residue, which dissolved with green color in concentrated hydrochloric acid on heating; when the solution cooled it became nearly colorless.

The same reactions occurred in an atomic weight determination of nickel, on washing the gold reprecipitated by sulphurous acid; by evaporating the wash-waters and dissolving in hydrochloric acid, a solution was obtained differing in its reactions from the chlorides of any known element.

The amount of chloride obtained in this way was very small. An attempt was made to obtain more by extracting nickel sulphide with yellow ammonium sulphide, and repeating this treatment for weeks; a residue was finally obtained quite insoluble in ammonium sulphide, which contained a much greater percentage of the new substance than the original nickel salt.

Various other methods were tried, till finally the observation that the new oxide, fused with alkaline hydroxides, dissolves in the fused mass, while cobalt and nickel oxide remain undissolved, pointed out the way to obtain the new oxide pure and in sufficient amount from either nickel or cobalt salts. From 50 grams of nickel oxide we obtained 1 gram pure new oxide.

Following are some of the characteristic reactions of the new element: The acidulated chloride solution is not precipitated by sulphuretted hydrogen; ammonium sulphide precipitates from the neutral solution a black sulphide; ammonia forms a very voluminous white precipitate resembling zinc hydroxide, insoluble in excess of ammonia; potassium hyroxide (½ normal solution) also precipitates white hydroxide quite insoluble in even a large excess of potassium hydroxide. This is a sharp distinction from aluminium hydroxide, no traces of which could be found in the new oxide. Ignited with cobalt solution, it does not yield Thenard's blue, but turns pale brown. When the oxide has been ignited for some time over the blast-lamp, it forms a soft white powder which dissolves readily in cold dilute hydrochloric acid. The strongly acid chloride solution shows the peculiar greenish yellow shimmer which first arrested our attention. When quite anhydrous and free from acid, the chloride is white and forms a colorless solution in water; but if hydrochloric acid vapor is blown over the chloride it turns greenish, and its solution in water is colored. When heated in a current of hydrogen the acid does not resemble nickel or cobalt oxides, for its weight remains unchanged even when submitted to violent ignition in an atmosphere of hydrogen. We have succeeded, however, in isolating the metal from which the white oxide is derived by electrolysis of an aqueous solution of the chloride. The metal was also obtained by drying the chloride in an atmosphere of carbon dioxide, and reducing it by hydrogen at red heat. The metal is black, in thin scales brownish black; if isolated by electrolysis, it is easily soluble in acids, but is soluble with difficulty after being heated to a high temperature in hydrogen.

Further communications will soon follow, and we now purposely refrain from all speculation regarding the atomic weight of cobalt, nickel, or the new metal, but we wish to reserve this field of work for the present.

REVIEWS AND REPORTS.

Recent Progress in Industrial Chemistry.

In a review of the most important directions in which chemical industries have been extended and developed during a given period, the aim should be to present a correct outline of those improvements in processes which have proved successful in actual practice. A list of patents and suggestions is of little interest, for but few of these ever come to actual trial on a large scale, and fewer still prove to be of permanent value. In the following pages the author has endeavored to follow the example of the able reports written for this journal ten years ago by Professor Mallet,[1] and to give prominence to the most important changes in industrial processes which have taken place since the above papers appeared.

1. Sulphuric Acid.

Materials of Sulphuric Acid Manufacture.—The first sulphuric acid manufactured was "fuming" acid, which was obtained in Bohemia by distilling ferric sulphate. The manufacture from sulphur was introduced in England in 1740. After that time sulphur was generally used until about 1833, when Perret & Sons, of Chessy, near Lyons, began to utilise in sulphuric acid-making the sulphur dioxide given off in the burning of copper ores. The monopoly of the exportation of Sicilian sulphur, granted in 1838 to a firm in Marseilles, though of brief duration, caused a general search for other sources of sulphur. Deposits of pyrites were developed in Westphalia, Hungary, France, Belgium, Ireland, and other countries, which supplied the wants of Europe for a long period. The pyrites from these sources has now been almost entirely supplanted by the cupreous pyrites of Spain and Portugal, which is burned chiefly for the copper and silver which it contains, with the production of sulphuric acid as a by-product. The use of sulphur for acid-making has been almost wholly abandoned in Europe. In 1887 there were imported into England 597,595 tons of pyrites, and only 32,624 tons of sulphur.

In the United States important deposits of pyrites occur, chiefly in New Hampshire, Massachusetts, and Virginia; the total quantity produced from these sources amounted in 1887 to 53,233 tons. During the same year there were imported from Canada about 35,000 tons, and from Spain 16,600 tons. The importation of sulphur from Sicily amounted in 1887 to 88,593 long tons. As these figures show, sulphur is still more generally used than pyrites in the United States for the manufacture of sulphuric acid. It was estimated[1] that in 1884 306,000 tons of acid were made from sulphur and 122,000 tons from pyrites. In 1887 only four additional works had taken up the use of pyrites. The reason of this delay in the introduction of pyrites on the part of American manufacturers is probably the great demand for sulphuric acid in this country for the manufacture of fertilizers and the refining of petroleum; the price of acid is therefore comparatively high, and the practice of rigid economy unnecessary. The introduction of pyrites has also to contend against the higher cost and more complicated working of the apparatus which its use involves. Another advantage of sulphur is that it produces acid free from arsenic, an important consideration if the acid is to be used in the manufacture of chemicals used in the preparation of food or medicines, though of no consequence in the petroleum or fertilizer industries. Further, when sulphur is used, the burner gases are somewhat richer than those from pyrites, since in the latter case a portion of the oxygen of the air admitted remains behind in the oxide of iron of the cinders. Lunge[2] calculates that one kilogram of free sulphur gives 6109 liters of gas, while the same weight of sulphur in the form of pyrites gives 8145 liters. This renders it necessary to provide one-fourth to one-third more chamber space for pyrites than for sulphur. There can, however, be no question that pyrites is decidedly the cheaper material, especially when the cinders are worked for copper. Dr. Francis Wyatt, in his valuable review of the development of American chemical industry,[3] estimates that by the manufacture of acid at the pyrites mines the cost might be reduced from $5.50 to $4.20 per ton of chamber acid. To compete with this, brimstone must be sold at $14 per ton, whereas the price in 1887 ranged from $19 to $24.

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[1] Mallet, The Progress of Industrial Chemistry. This Journal **9** and **10**.

Generally speaking, works near Philadelphia and in the South are still using sulphur, while in the more complete and modern plants in the neighborhood of New York and in New England pyrites is employed.

Extraction of Sulphur.—The methods of extracting sulphur from the gangue in Sicily have been greatly improved in recent years by the introduction of larger kilns for burning the ore. According to Consul Carroll,[4] these have in some cases the capacity of 5000 tons each, and the smelting operation requires several months for its completion. In these kilns from two-fifths to three-fifths of the sulphur contained in the ore is obtained, or from two to three times as large a proportion as in the small kilns formerly used. More perfect methods of extraction are employed in Sicily to some extent, but owing to the scarcity of fuel, costliness of machinery, and lack of intelligent labor, the greater part of the sulphur is still obtained by means of the "calcaroni" or large kilns. According to Vincent,[1] the process of Tour and Debreuil has been introduced into Sicily. This consists in immersing the ore, contained in iron baskets, in a solution of calcium chloride heated to 130° C., or above the melting point of sulphur. By this process it is possible to extract all but four or five per cent. of the sulphur contained in the ore. Consul Carroll states that Durand's process of fusion in iron pots and ladling out the melted sulphur, Hirzel's furnace, Thomas's process of fusion by superheated steam, and Bollmann's method of extraction by carbon disulphide, are also to some extent used.

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[1] Mineral Resources of the United States, 1883-4.

[2] Sulphuric Acid and Alkali, Vol. 1, p. 240.

[3] Engineering and Mining Journal, 1887, and Mineral Resources, 1886, p. 671.

[4] U. S. Consular Reports, No. 92, 1888, p. 182.

In the United States sulphur is obtained on a commercial scale only at Cove Creek, Utah. The deposits are stated to be very extensive, and the production of sulphur has rapidly increased during the past few years. In 1887 the amount obtained was about 3000 tons. The sulphur is extracted by fusion with superheated steam. Cedar wood for fuel is abundant and cheap.

Pyrites Burners.—The furnaces used for burning pyrites have been often described, and no important changes have been lately introduced. The forms generally used in Europe and this country are grate-burners for lump ore, and shelf-burners for "smalls." The "Spence Mechanical Furnace," now largely used in Europe and at some works in this country, is a shelf-burner for small ore in which the charge is pushed from one shelf to another by steam-power instead of by hand.

Utilisation of Pyrites Residue.—With modern burners for smalls, and especially with the Spence furnace, it is possible to burn the pyrites down to one per cent. of sulphur. The resulting cinders from non-cupreous pyrites consist chiefly of ferric oxide, and are almost absolutely free from phosphorus. Such cinders are valuable as iron ore. According to Dr. Wyatt, several acid works near New York are now selling their non-cupreous pyrites cinders to iron-smelters at three or four dollars per ton.

Cinders from pyrites containing notable quantities of copper are treated by the wet extraction process. If much silica and little silver are present, as in the case of cinders from most kinds of American pyrites, it is found best to smelt the cinders with the addition of raw pyrites in the form of "fines," and thus to obtain a "matte" containing 50 to 60 per cent. of copper. By this method, however, the iron and silver contained in the cinders are lost. If, on the other hand, there are present two or three ounces per ton of silver and but little silica, as is generally the case with the cinders from Spanish ores, the Henderson wet process is used for the extraction of copper and silver.

It is stated that 400,000 tons of pyrites residue are annually treated by this process in England alone. The cinders are roasted with salt, sometimes with the addition of the mattes obtained by smelting siliceous ores. The cinders contain copper chiefly in the form of sulphate and sulphide. After the roasting with salt the copper is principally in the form of chloride, with a considerable proportion of oxide. Hydrochloric acid is given off during the roasting, and is condensed in the usual way. The resulting cinders are lixiviated, first with water, then with the dilute acid obtained in the operation. In the solution the silver is precipitated by potassium iodide or hydrogen sulphide, and the copper by scrap iron. This process is worked to some extent in this country, using the residues from Spanish pyrites, at Elizabeth, N. J., Natrona, Pa., and probably at other places.

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[1] Trans. by Bayley, this Journal **6**, 63.

Modern Acid Works.—The use of the Glover Tower has become general in Europe, but has not been taken up by more than one-half the works in this country. Near New York and in New England, however, are located several new works at which highly concentrated acid for use in refining petroleum and in making nitro-glycerin is made. These establishments are generally equipped with all the best appliances, such as shelf-burners for smalls, Glover and Gay-Lussac towers, and platinum concentrating apparatus, and are as complete and perfect as any works in Europe.

Concentration of Sulphuric Acid.—The chamber acid has generally a strength not above 50° B., corresponding to about 62 per cent. of H_2SO_4. This is strong enough for the manufacture of superphosphates, ammonium sulphate, and even for the salt-cake process. For the refining of petroleum, the manufacture of nitric acid, and especially in making nitro-compounds, acid of greater strength is needed. Acid from the Glover tower may reach a strength of 62° B., corresponding to 81.7 per cent. of H_2SO_4. Beyond this point the concentration must be carried on in platinum stills or glass retorts. Acid from the Glover tower cannot generally be concentrated in platinum, since it contains a large amount of ferric sulphate, which would deposit on the pan and do serious damage. When platinum stills are used, therefore, acid from the chambers is first concentrated in lead pans by the waste heat of the platinum stills or burners to 60° B., then run into the stills. In this country these are generally on the Faure and Kessler system, and consist of a pan of platinum, surmounted by a leaden dome cooled by a water-jacket. The great drawback to the use of platinum is its rapid corrosion, which is especially marked in the case of acid containing nitrogen compounds or considerable quantities of arsenic. Acid made from sulphur is free from arsenic, and that made from American pyrites is practically so. The oxides of nitrogen must be completely removed before distillation in platinum is attempted. This is done by the addition of a little ammonium sulphate, which decomposes the nitrogen compounds, forming water and free nitrogen.

According to W. H. Adams,[1] platinum stills would last almost indefinitely for the concentration of acid free from arsenic up to a strength of 65° B., or about 90 per cent. H_2SO_4. Such acid is strong enough for almost all purposes, but for the manufacture of nitro-benzene, nitro-glycerin, etc., further concentration is necessary. Beyond this point lead, iron and other substances are rapidly precipitated and adhere to the bottom of the pan, causing its speedy destruction, and it is in the removal of the last portions of water that the chief injury to the apparatus takes place. Within the last few years cast-iron retorts have been successfully used for the final concentration, and are now employed on a large scale in extensive works near New York. It is found that acid of 65° B. does not attack the stills, and no injury appears to result from the deposition of arsenic or other substances. The concentration is carried as far as possible in platinum; the acid is then run into the cast-iron stills and concentrated to 98 per cent. H_2SO_4. It is stated by Mr. Adams that a set of iron stills such as he describes is in use near New York in connection with platinum, and is producing 30,000 pounds per day of 98 per cent. acid.

In England the use of glass seems to be increasing, owing to the cheapness and perfection of the large retorts which are now made. By the use of glass, acid from the Glover tower may be concentrated directly, and no injury results from the presence of arsenic or nitrogen compounds. The final concentration, however, presents many difficulties, owing to the violent ebullition of the strong acid and the separation of sediments. The loss by breakage is therefore still very great.

SPENCER B. NEWBURY.

DETERMINATION OF CARBON MONOXIDE IN GAS-MIXTURES.

The determination of carbon monoxide in gas-mixtures is usually effected by absorption in an ammoniacal[2] or a hydrochloric acid[3] solution of cuprous chloride. But it has been observed[4] that the volume of certain gases which contain but little monoxide is often increased, instead of diminished, by agitation with solutions of cuprous chloride. This increase of volume Hempel[5] ascribed to a failure on the part of the operator to remove the heavy hydrocarbons by strong sulphuric acid, before proceeding to a determination of the carbon monoxide. It was assumed that the solution of cuprous chloride, having absorbed heavy hydrocarbons which should have been taken out by sulphuric acid, was forced to give them, or a part of them, up again when agitated with a new portion of gas in which the carbon monoxide was to be determined, and thus it might happen that a gas containing but little carbon monoxide would increase in volume when treated for its removal. This explanation was declared by Drehschmidt[1] to be insufficient and even erroneous, since the increase in volume referred to is often observed even after the removal of the heavy hydrocarbons by sulphuric acid. It is then suggested that the expansion is due to the feeble union of the carbon monoxide and cuprous chloride; in other words, that a solution of cuprous chloride containing carbon monoxide may give up a portion of the latter to any gas with which it is agitated. Moreover, it was found in every case of such increase of volume, that the presence of carbon monoxide in the gas could be established by combustion with palladium asbestus or by explosion.

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[1] Twenty Years' Progress in the Concentration of Sulphuric Acid; Proc. of Amer. Inst. of Mining Engineers, 1887.

[2] Hempel's Neue Methoden zur Analyse der Gase, p. 40.

[3] Winkler's Anleitung zur Untersuchung der Industriegase **1**, 38.

[4] Ber. d. chem. Ges. **20**, 2344.

[5] Ber. d. chem. Ges. **20**, 2344.

It was also found that the absorption of carbon monoxide by cuprous chloride is rarely complete; never so, in fact, except when perfectly fresh solutions are employed; and that the amount which remains unabsorbed depends upon the quantity of carbon monoxide previously absorbed by the cuprous chloride, and upon the volume of the non-absorbable gas. It appeared also that the quantity remaining unabsorbed is greater when the hydrochloric acid solution is used, and that for this reason the ammoniacal solution is to be preferred. If the gas is allowed to stand over the liquid, the quantity of carbon monoxide in the gas diminishes with time in the case of the ammoniacal, but not in the case of the acid solution. The author explains this by the fact that carbon monoxide slowly precipitates metallic copper from ammoniacal cuprous solutions. He recommends that the gas, from which most of the carbon monoxide has been removed, be again agitated with a fresh solution of cuprous chloride, or that it be mixed with air and passed over heated palladium asbestus.

Hempel[2] admits that a solution of cuprous chloride may, under certain circumstances, give off gas, but he believes it to be improbable that a solution which is easily capable of absorbing four times its own volume of the gas should, when only partially saturated, give up carbon monoxide to another gas which is only slightly soluble in it. He therefore endeavors to find in the conduct of the gases, which are only mechanically absorbed by the solution, an explanation of the increase of volume. He says, in effect, that when, as in the experiments of Drehschmidt, the copper solution is treated (1) with a mixture of carbon monoxide and nitrogen, (2) with hydrogen and then (3) with a mixture of carbon monoxide and nitrogen, and (4) with nitrogen, it will first absorb nitrogen (1), which will for the most part be again given up when the solution is treated with hydrogen, and that the last will be in turn displaced by nitrogen (3 and 4). These facts, he says, explain without any difficulty the observations of Drehschmidt. He wholly ignores the evident fact that whether in the case given there will be expansion or contraction, or no change in volume, will depend upon the relative solubility of nitrogen and hydrogen; and that, if there is expansion when the nitrogen is displaced by hydrogen, there must be contraction when the hydrogen is in turn displaced by nitrogen.

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[1] Ber. d. chem. Ges. **20**, 2752.

[2] Ibid. **21**, 898.

He remarks very justly that it is not permissible to employ the same absorbing liquids for the analysis of gases of widely differing composition; but that the errors which would be thus introduced may be obviated by repeating the analysis with a fresh portion of the gas. For a like reason, analyses made with entirely fresh absorbing liquids are not correct, and must be repeated. Drehschmidt,[1] in order to test the correctness of Hempel's explanation, treated solutions of cuprous chloride containing carbon monoxide with pure nitrogen. In each case an increase of volume was observed; and that this increase was due to carbon monoxide derived from the solution was proved by mixing the gas with oxygen and exploding, or by burning by means of palladium asbestus, and absorbing the carbon dioxide. He concludes that, in order to obtain sufficiently correct results with Hempel's apparatus, it is necessary to employ two absorption pipettes for the determination of carbon monoxide, one of which shall always contain a comparatively fresh solution of the cuprous chloride. Otherwise, the gas is to be mingled with air and the mixture passed over heated palladium asbestus.

H. N. Morse.

THE ORIGIN OF PETROLEUM.

An interesting contribution to the evidence of the animal origin of petroleum has recently been made by C. Engler.[2] There are two theories concerning the origin of petroleum; the first, the so-called emanation theory, assumes petroleum to be generated by chemical decomposition of inorganic matter, in the heated interior of the earth; according to the second theory, petroleum is formed by the decomposition of vegetable or animal matter. Several hypotheses have been suggested by different chemists in support of the emanation theory, the most prominent being that of Mendelejeff, who thinks that water penetrating through crevices comes in contact with highly heated carburets of iron and other metals in the earth's pyrosphere, forming metallic oxides and gaseous hydrocarbons, which condense to petroleum in the cooler portions of the earth's crust. While it is true that Mendelejeff and other chemists before him have succeeded in obtaining mixtures of hydrocarbons resembling petroleum, by reactions in the laboratory similar to those supposed, the weight of geological and paleontological evidence is against all theories which assume an inorganic source of petroleum, and points to marine animal life as the probable source.

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[1] Ber. d. chem. Ges. **21**, 2158.

[2] Ber. d. chem. Gesell. **21**, 1816.

Recently Krämer and Böttger,[1] in a study of the hydrocarbons contained in crude petroleum, advanced the opinion that certain of these hydrocarbons must have been formed by distillation of organic matter at comparatively low temperature and high pressure. Engler had at this time opportunity to use an apparatus designed for factory work, in which he could distill large quantities of liquid under a pressure of two atmospheres. Influenced by Krämer's suggestion, he distilled 1000 lbs of menhaden oil at a temperature of 350°–400° and a pressure of two atmospheres. The distillate consisted of combustible gases, water, and 600 lbs of oil resembling crude petroleum in appearance and reactions. Of this oil 26 per cent. boiled below 150°, 58 per cent. between 150° and 300°, 16 per cent. above 300°. The two higher boiling portions have not yet been examined. By fractional distillation of the portion boiling below 150°, Engler has thus far isolated pentane, hexane, heptane, octane and nonane of the paraffin series, and finds that hydrocarbons of the secondary series are also present; in short, this oil seems identical with that portion of crude petroleum boiling below 150°. As fish oil is a mixture of triglycerides, chiefly of oleïc and stearic acids, Engler thought it of interest to distill chemically pure triglycerides of these acids, and the free acids under pressure. As apparatus he used thick glass tubes bent at an obtuse angle, in each of which he put 30 grams of substance, and sealed the tubes, placing them in a digestor so that the empty ends hung downward outside the digestor. After heating for four hours at 350°, the tubes were cooled and opened, to allow the escape of gases; then resealed and again heated. This treatment was continued till the reaction seemed finished. Triolein yielded a product of which 50 per cent. boiled below 150°; tristearin 60 per cent., oleïc acid 60 per cent., stearic acid 60 per cent. Engler found that the triolein under proper conditions left no residue, but was entirely changed into gases, water, and volatile oil.

To explain the fact that crude petroleum contains only traces of nitrogen, Engler assumes that on the decomposition of the animal remains under long continued pressure, the nitrogen escapes as ammonia, and refers to the work of Gregory[2] and Wetherill[3] on the formation of adipocere.

An objection urged against the organic origin of petroleum is that no free carbon is found in crude petroleum. Engler takes up this hitherto unanswered point and shows that if all of the oxygen of the triolein or tristearin should combine with part of the hydrogen to form water, 87 per cent. carbon and 13 per cent. hydrogen would remain.

[1] Ber. d. chem. Gesell. **20**, 595.

[2] Ann. Chem. (Liebig) **61**, 362.

[3] Transactions of the Amer. Philosoph. Soc. **11**.

The numerous analyses by St. Clair Deville and Markownikoff and Oglobin, of the American, European and Caucasian petroleums show that crude petroleum contains an average of 87 per cent. carbon and 13 per cent. hydrogen—certainly a striking coincidence!

EDWARD RENOUF.

THE CONSTITUTION OF BENZENE.

An article by H. Sachse,[1] entitled, "Ueber die Configuration des Benzolmoleküls," has recently appeared. The author comes to the same conclusion as Kékulé, viz., that the only solution of the problem can be found in a consideration of the space relations of atoms, as laid down by Van't Hoff and Wislicenus. In accordance with this hypothesis, he considers the carbon atom situated at the center of a regular tetrahedron, with its points of affinity situated at the four corners thereof, and exerting its four equal affinities in the directions of these points. He also thinks that the atoms of other elements are similarly situated at the centers of other geometrical figures, whose form is conditioned by the number and directions of the affinities of the respective atoms. If the carbon atoms of the formulas of Kékulé, Ladenburg or Claus be replaced by tetrahedrons, figures will result which will not satisfy all the conditions required by facts, and especially will they show no reason why six, and just six, such tetrahedrons should give the most stable form of combination, and why in the combination of two benzene rings, in their most stable form of combination, they should have two carbons in common, as we have in naphthalene, anthracene, and most of the high-melting products of the distillation of coal-tar. He hence concludes that there must be a union of affinities in benzene which is peculiar to this and to all rings derived from it. This condition he thinks is represented in his conception of the structure of benzene, which also gives a reason why six atoms represent the stablest form of combination, and why two rings do have two atoms in common as above stated. His conception can best be understood by the study of a model constructed as follows: An octahedron—one of pasteboard is the best—has any two of its triangular faces, which are parallel, removed. Upon each of the remaining triangular faces a tetrahedron, whose faces are of the same size as those of the octahedron, is attached, face to face. Thus a figure will result which has six free corners, one from each tetrahedron, which represent the six free affinities of benzene. An examination of this figure will show that neither the molecule nor even one carbon atom can become saturated without changing the entire system. In this respect it is like Kékulé's formula.

The six-membered ring thus formed is the most stable of all rings formed of any number of carbon atoms, because each atom is so combined with its neighbor that it is in stable equilibrium, and because the system can only move as a whole, no periodic vibrations of separate carbon atoms being possible. The latter is evident from the model, and the former is proved geometrically as follows:

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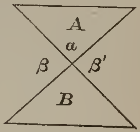
[1] Ber. d. chem. Gesell. **21**, 2530.



If *A* and *B* be the projection upon the plane of the paper of two tetrahedrons joined by double union as they are commonly represented according to the Van't Hoff hypothesis and as they actually occur in the model, then to be in equilibrium β must be equal to β', whence follows $\beta = \frac{360° - 2\alpha}{2}$, where α is the angle of the tetrahedron, which is 70° 32′. By substituting this for α in the formula, we obtain $\beta = 109° \ 28' = \beta'$. But this is just the angle of an octahedron, whence, as the inside of our model is an octahedron, it follows that each of the six tetrahedrons is so combined with its neighbor that $\beta = \beta'$ (the exterior and interior angles of our model) for each pair, and that they are hence in stable equilibrium.

From $\beta = \beta'$ it also follows that there is a possibility of another ring similar to our model being added to it, which must have two tetrahedrons in common with the former, as β is the solid angle between any two of them. In this conception we have only double union of carbon atoms, which the author terms "edge-combination,"[1] as two tetrahedrons are then in combination by a common edge. This would not be possible according to our conception of the distribution of affinities in benzene, inasmuch as six carbon atoms united each by two affinities to its neighbor would leave no free affinities with which the hydrogen atoms of benzene could enter into combination. But this is where the author introduces his new conception of the union of carbon atoms peculiar to benzene and ring formation in general, above alluded to. It is this: When two carbon atoms are combined by double union, the affinity from each directed to one of the common points of union does not completely neutralise that from the other atom directed to the same point, as they meet at an angle. Hence a third affinity from a third adjacent carbon atom is used in completing the mutual neutralisation. Hence at any and every point on the model where three carbon atoms meet we have this distribution of affinities, and it is this distribution which is peculiar to ring-formation, and in particular to benzene.

For the facts which he mentions in favor of his hypothesis, reference must be made to the original article.[2] One, however, may be mentioned here, as it involves another new conception in regard to the relative distances of ortho, meta and para positions. It is the fact that ortho-dioxy-benzene compounds do not form anhydrides. If x is the distance between any two corners of a tetrahedron, *i. e.* points of affinity, then by calculation it is found that the distance in the model between the free points of affinity of two ortho, meta or para atoms respectively is represented by

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[1] "Kantenverbindung."

[2] Loc. cit. 2534.

$$o = \sqrt{2}x \qquad m = 2x \qquad p = \sqrt{6}x$$

$$\text{or } o^2 : m^2 : p^2 = 1 : 2 : 3.$$

Let us apply this to the problem. The distance between the two affinities of an oxygen atom must be the same as between those of a carbon atom, *i. e.* $= x$, as is shown in compounds containing $C = O$, or carbonyl oxygen. Hence the greatest distance that an oxygen atom in combination with carbon can span, so to speak, is x. But according to the theory, the two ortho points of affinity must be separated by a distance represented by $\sqrt{2}x$, which is greater than x, and as the carbon atoms are immovable, the anhydride cannot be formed. In case of salicylic acid, where there is a side chain, bending can take place, and an anhydride, salicylide, can be formed. Sachse proposes in a later article to apply his hypothesis to addition-products, quinones, and other derivatives of benzene.

A. R. L. DOHME.

THE MOLECULAR FORMULAS OF SOME METALLIC CHLORIDES AND SIMILAR COMPOUNDS.

In view of the recent developments in the study of the specific gravity of the vapors of metallic chlorides, the following article, in which a brief account is given of all such determinations which have been made, may prove of service.[1]

Aluminium Chloride.—In 1857, Deville and Troost[2] made five determinations of the vapor density of aluminium chloride by Dumas' method. Two at 350° gave 9.38, 9.35, and three at 440° gave 9.33, 9.34, 9.37, which correspond very well with the theoretical density 9.3 for Al_2Cl_6.

In 1860 Cahours[3] analysed the methyl and ethyl compounds of aluminium, and as a result proposed the formulas $Al(CH_3)_3$ and $Al(C_2H_5)_3$. The vapor densities of these compounds were determined in 1865 by Buckton and Odling,[4] using Gay-Lussac's method. One experiment on aluminium ethyl at 234° gave 4.5, the theory for $Al(C_2H_5)_3$ requiring 3.9. Two experiments on aluminium methyl at 220° and 240° gave respectively 2.8, 2.8, the theory requiring for $Al(CH_3)_3$ 2.5. Experiments ranging from 140° to 163° gave figures ranging from 4.4 to 4.1. The authors concluded that the vapor of the latter compound was anomalous.

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[1] This paper was finished and in the hands of the editor of this Journal before the paper by Sidney Young on the same subject appeared in Nature (see Nature **39**, 198).

[2] Ann. chim. phys. (3), **58**, 257.

[3] Ibid. (3), **58**, 22.

[4] Ann. Chem. (Liebig), Suppl. **4** (1865), 111.

Near its boiling point, 140° C., its density corresponds to the double molecule, while above 220° it corresponds to the simple molecule.

In 1879, Victor Meyer,[1] by his own method, using an atmosphere of nitrogen, experimented on the density of aluminium chloride at 697°, but his results were uncertain, on account of the dissociation which the compound suffered. He suggested that this difficulty might be overcome by using an atmosphere of chlorine.

In 1887,[2] Nilson and Petterson, by Meyer's method, working in nitrogen at 440° and 458°, obtained respectively 7.79 and 4.8. Between 458° and 943° the result remained practically 4.5, which is very close to 4.6 required for $AlCl_3$. Above 943° dissociation was observed, the vapors attacking the platinum vessel.

In 1888, Friedel and Crafts,[3] by Dumas' method, made 21 determinations of the vapor density of aluminium chloride, under variations of temperature and pressure. Twelve experiments at 760 mm. between 218° and 400° gave an average result of 9.36; five at 1520 mm. and below 400° gave an average of 9.32. The remaining experiments made above 400° gave 8.6, which the authors attributed to dissociation. They also suggested that dissociation is favored by the use of inert gases in Meyer's method.

The work on the hydrocarbon compounds of aluminium was taken up again by Roux and Louise[4] in 1888. Using Meyer's method with nitrogen, they made two experiments on aluminium methyl at 182° and obtained 5.08 and 5.15, the theory for $Al_2(CH_3)_6$ requiring 5.02. Two experiments at 216° gave 4.78 and 4.7; two at 350°, 2.33 and 2.55; two at 440°, 1.94 and 1.68. The authors claim that the compound vaporises undecomposed at 182°, 42° above the boiling point, but at higher temperatures dissociates. Similar results were reached with the ethyl compound. At 235°, 35° above the boiling point, 8.15 and 7.99 were obtained in two determinations. The theory for $Al_2(C_2H_5)_6$ requires 7.92. At 258° three experiments gave 6.41, 6.35 and 6.04; at 310°, 2.1; at 440°, 1.3. Above 250° dissociation occurred. Several determinations were made by Raoult's method, using ethylene bromide as the solvent. Three results obtained with the ethyl compound gave 240, 234 and 229 for the molecular weight, figures which are fairly near 229 required for $Al_2(C_2H_5)_6$. The results obtained with the propyl and isoamyl compounds were very discordant, in consequence, no doubt, as claimed by the authors, of the presence of impurities.

The work done by Deville and Troost[5] in 1857 on aluminium bromide and iodide has not been repeated. Their results, 18.62 and 27, agree fairly well with 18.51 for Al_2Br_6 and 28.3 for Al_2I_6.

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[1] Ber. d. chem. Gesell. **12**, 1199.

[2] Ztschr. phys. Chem. **1**, 459.

[3] Compt. rend. **106**, 497.

[4] Bull. Soc. chim. (Paris), 1888, 497.

[5] Ann. chim. phys. (3) **58**, 257.

Beryllium Chloride.—In 1884, Nilson and Petterson,[1] working by Meyer's method in carbon dioxide, made a series of experiments between 686° and 812°. The densities found varied from 2.75 to 2.93. In 1885[2] a more extended series was made, varying from 686° to 1502°, giving densities varying from 2.7 to 2.85. The theory for $BeCl_2$ requires 2.77.

Chlorides of Chromium.—The only work done on these compounds is that by Nilson and Petterson,[3] 1888. The trichloride volatilises normally between 1190° and 1277°, giving an average density of 5.5, the theory for $CrCl_3$ requiring 5.48. Above 1300° dissociation was observed. The dichloride was very difficult to volatilise. From 1300° to 1400° the density 7.8 was found; at 1500°, 7.3; and at 1600°, 6.23. The authors think the theory 4.26 for $CrCl_2$ may be reached at higher temperatures.

Cuprous Chloride.—In May, 1880, V. and C. Meyer[4] tried the vapor density at a bright red heat and found it to be 7.05, the theory for Cu_2Cl_2 requiring 6.84. The scientific world questioned this result, so in June[5] of the same year the experiment was repeated at 1560° and the figure 6.93 obtained.

Ferrous Chloride.—Victor Meyer, 1879,[6] using his own method with nitrogen, made some experiments on ferrous chloride at a temperature not given, and found that the salt broke up into the metal and ferric chloride. He suggested that in an atmosphere of hydrochloric acid gas this would not occur, and in 1884[7] made the determination at a bright yellow heat. Two densities were found, 6.67 and 6.38, lying midway between 4.39, the theory for $FeCl_2$, and 8.78 for Fe_2Cl_4. There was no dissociation.

In 1888, Nilson and Petterson,[8] by Meyer's method, made a series of experiments between 1300° and 1500°, and obtained densities varying from 4.34 to 4.30.

Ferric Chloride.—In 1860, Deville and Troost[9] made two determinations of the vapor density of ferric chloride by Dumas' method, in a bath of sulphur, obtaining the figures 11.37 and 11.42. Theory for Fe_2Cl_6 requires 11.27.

Victor Meyer,[10] in 1879, made the same determination by his own method, in an atmosphere of nitrogen. At 448° he obtained 11.14, and at 619°, 11.01. Dissociation was observed at higher temperatures. In 1888 he and Grünewald[11] repeated the work, making twenty-two determinations in an atmosphere of nitrogen, and four in chlorine. At 448° four experiments in nitrogen gave an average of 10.49, and two in chlorine gave 10.65. Three experiments in nitrogen at 518° gave an average of 9.57. At the same time, however, the salt had decomposed, yielding 10 per cent. of ferrous chloride. Two experiments in chlorine at the same temperature gave an average of 8.74. In nitrogen, as the temperature rose above 518°, the dissociation increased correspondingly, reaching 33 per cent. at about 750°. Nevertheless the authors conclude, especially from the results in chlorine, that the molecule Fe_2Cl_6 does not exist.

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[1] Ber. d. chem. Gesell. **17**, 987.

[2] J. prakt. Chem. **33**, 13.

[3] Ztschr. phys. Chem. **12**, 674.

[4] Ber. d. chem. Gesell. **12**, 1116.

[5] Ibid. **12**, 1283.

[6] Ber. d. chem. Gesell **12**, 1199.

[7] Ibid. **17**, 1335.

[8] Ztschr. phys. Chem. **2**, 671.

[9] Ann. chim. phys. (3), **58**, 283.

[10] Ber. d. chem. Gesell. **12**, 1199.

[11] Ber. d. chem. Gesell. **21**, 687.

Friedel and Crafts[1] were engaged on the same problem in 1888, under the influence of diminished pressure and low temperature. Between 356° and 442° several experiments in chlorine and at 760 mm. gave densities varying from 11.30 to 12.04. At 325° and 407.4 mm., 12.47, and at 321° and 377.4 mm., 11.41. Dissociation was not observed in any of the work. In an atmosphere of nitrogen, however, at 760 mm., dissociation occurred at 433° and 432.7°, giving 10.75 and 10.97.

Gallium Trichloride.—In 1880, Lecoq de Boisbaudran,[2] by Dumas' method, determined the vapor density at 440°, 357°, 273°, and 247°, to be respectively 7.8, 10, 11.9 and 13.4. The theory for Ga_2Cl_6 is 12.16. Friedel,[3] in 1881, by Meyer's method at 440°, 357° and 440°, found 7.8, 8.5 and 6.6. In 1888, Friedel and Crafts[4] repeated the work in nitrogen and under increased pressure. At 307° and 760 mm. they obtained 10.6; at 357° and 760 mm., 9.1; at 377° and 1090 mm., 7.8; at 237° and 1138 mm., 11.73. Dissociation was observed at higher temperatures.

In 1888, Nilson and Petterson,[5] by Meyer's method, at 350° obtained 8.85; between 440° and 606°, 6.12 and 6.14 were obtained, but at higher temperatures the salt decomposed. They throw out the figure obtained at 350° and conclude that the two results obtained at 440° and 606° settle the question as to the molecular weight.

At the same time they prepared some gallium dichloride and determined its vapor density. Between 1000° and 1100° they obtained 4.8. The calculated figure for $GaCl_2$ is 4.86. Above 1300° the salt decomposed.

Chlorides of Indium.—In 1879, Victor Meyer[6] determined the density of the vapor of the trichloride to be 7.87. The theory for $InCl_3$ is 7.55. At the bright red of the experiment no dissociation was observed.

Although other chlorides were believed to be possible, the trichloride was the only one known until 1888. In that year Nilson and Petterson[7] showed the existence of the dichloride and the monochloride. The vapor densities of the three chlorides were taken by Meyer's method. The trichloride between 606° and 850° gave figures varying from 8.16 to 7.39; and between 1048° and 1200°, 6.72 to 6.23. The fall in density was attributed to dissociation above 1000°. The dichloride between 1167° and 1400° gave 6.55–6.43, figures which agree very well with the theory for ICl_2, which is 6.36.

The monochloride between 1100° and 1400° gave 5.3–5.5, the theory for ICl being 5.14.

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[1] Compt. rend. **107**, 301.
[2] Compt. rend. **93**, 326.
[3] Loc. cit.
[4] Ibid. **107**, 306.
[5] Ztschr. phys. Chem. **2**, 666.
[6] Ber. d. chem. Gesell. **12**, 611.
[7] Ztschr. phys. Chem. **2**, 650.

Stannous Chloride.—In 1870,[1] Reith, using a Hofmann's furnace, made two experiments on the vapor of stannous chloride (temperature not mentioned), and obtained 7.47 and 6.88. The theory for $SnCl_2$ is 6.53. In 1879, V. and C. Meyer,[2] in two determinations by Meyer's method at 619° and 697°, found 12.85 and 13.08, which agree very well with 13.06, the theory for Sn_2Cl_4.

V. Meyer and Züblin[3] repeated the experiments in 1880 and found at 800°, 7.22; at 880°, 6.67; and at 970°, 6.23. The glass vessel was attacked by the vapors, but no dissociation was observed. The authors suggested the existence of two modifications of the compound. Between 619° and 697° the vapor density leads to the molecular weight for Sn_2Cl_4, and this breaks down to two molecules of $SnCl_2$ between 800° C. and 970° C.

Biltz and Meyer[3] repeated these experiments in 1888, this time using an atmosphere of nitrogen. Five determinations were made at small intervals of temperature between 639° and 790°. They obtained the following figures: 8.76, 8.57, 8.49, 8.26, 7.7. The sixth experiment was made at 1113° and gave 7.1. The gradual sinking of the density without dissociation of the gas led the authors to assume that at a higher temperature the theory for $SnCl_2$, 6.53, would be reached.

Thorium Chloride.—From analyses of potassium thorium sulphate, Berzelius in 1827 assumed the formula of the oxide to be ThO. In 1852, Bergmann wrote the formula Th_2O_3, because of similarities to zirconium oxide, which he regarded as a sesquioxide Zr_2O_3. In 1857, however, Deville and Troost[4] showed that from the density of the vapor of zirconium chloride, its oxide should be written ZrO_2. Rammelsberg in 1860, and others later, showed that from the many analogies of the oxide of thorium to the oxides of silicon, titanium, and tin, its formula must be ThO_2. In 1885, Troost[5] determined the vapor density of the chloride of thorium by Meyer's method, using a bath of zinc. Three trials gave 5.9, 7 and 7.09. The theory requires 12.93 for $ThCl_4$. In 1887, Krüss and Nilson[6] repeated the experiments by Meyer's method, in an atmosphere of carbon dioxide. Between 1000° and 1270° figures varying from 11.2 to 12.4 were found. At 1400° dissociation was observed.

P. S. Baker.

Grünwald's Mathematical Spectrum Analysis.

Dr. Anton Grünwald, Professor of Mathematics in the Technical High School at Prague, has given his theory of spectrum analysis in the following papers: (1) Ueber das Wasserspectrum, das Hydrogen- und Oxygenspectrum: *Astronomische Nachrichten*, No. 2797, 1887, and Phil. Mag. **24**, 354, 1887; (2) Math.

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[1] Ber. d. chem. Gesell. **3**, 618.
[2] Ibid. **12**, 1195.
[3] Ber. d. chem. Gesell. **13**, 811.
[4] Compt. rend. **45**, 824.
[5] Ibid. **101**, 360.
[6] Ztschr. phys. Chem. **1**, 305.

Spectralanalyse des Magnesiums und der Kohle: *Monatshefte für Chemie* **8**, 650; Wiener Sitz. Berichte, II Abth. **96**, 1887; Phil. Mag. **25**, 343 (1888), (abstract); and (3) Math. Spectralanalyse des Kadmiums: *Monatshefte für Chemie* **9**, 956.

His aim is to discover relations between the elements by tracing connections between their spectra, and thus to arrive at simpler, if not fundamental "elements." He considers the lines in the spectra of two substances, say A and B. If he finds a group of lines in the spectrum of A which, on multiplication with a simple numerical factor, gives line for line a group in the spectrum of B, he assumes that A and B have a common component. This factor which transforms the one group into the other is, he says, the ratio of the volumes occupied by the common constituent in unit volume of the two substances. Thus, let c be common to A and B, and let it occupy the volume $[a]$ in unit volume of A, and $[b]$ in unit volume of B; then the factor which transforms that part of the spectrum of A due to c into that of B also due to c is $[b]/[a]$.

It is not difficult to find relations between the spectra of different substances; and, accepting Dr. Grünwald's hypothesis as to the transforming factor, we can deduce formulas for the elements. For example, in the hydrogen spectrum there are two groups of lines, $[a]$ and $[b]$, which, when multiplied respectively by $\frac{19}{30}$ and $\frac{4}{5}$, give corresponding groups in the spectrum of water, and, since in water hydrogen occupies $\frac{2}{3}$ of the volume, we have the equations:

$$[a] + [b] = 1$$
$$\tfrac{19}{30}[a] + \tfrac{4}{5}[b] = \tfrac{2}{3}$$
$$\therefore \quad [a] = \tfrac{4}{5}, \quad [b] = \tfrac{1}{5},$$

which gives hydrogen the composition ba_4. For reasons which depend upon solar physics, Grünwald calls the substance a coronium, and b helium. Further, he says that all the lines in Hasselberg's secondary spectrum of hydrogen can be changed into water-lines by multiplying by $\frac{1}{2}$; which shows, according to his theory, that the modified molecule H′ occupies in H_2O half the volume it does in the free condition. He finds that oxygen has the composition $H'b_4(b_4c_5)_5$, where c is a new substance. In his last paper, however, Dr. Grünwald states that he has proved c to be nothing but a in a different state of compression.

He adopts the spectrum of water, *i. e.* of the oxyhydrogen flame, as a standard, and is then able to give various criteria by means of which the primary elements a and b may be recognised. Among them are the following: If λ is the wave-length of any line produced by a as it exists in hydrogen, $\frac{19}{30}\lambda$, $\frac{3}{4}\lambda$, $\frac{56}{75}\lambda$ will each be the wave-length of a line of the water-spectrum; and if λ is the wave-length of any line produced by b as it exists in hydrogen, $\frac{4}{5}\lambda$ will be the wave-length of a line of the water-spectrum. Applying his criteria to magnesium, carbon, and cadmium, he finds that they are made up entirely of a and b in various states of compression. For instance, one group of lines in the cadmium spectrum is transformed into a group of *b* by the factor $\frac{2}{3}$, another group is identical with a group of *b*, and so on. But the group of lines of *shortest* wave-length is transformed into a group of *b* by the factor $\frac{7}{6}$; and cadmium falls in the 7th row of Mendelejeff's Table. Similarly, the group of lines of shortest wave-length of zinc is transformed into a group of *b* by the factor $\frac{5}{4}$, and zinc is in the 5th row of the table. Dr. Grünwald finds in this a general law which he verifies in the cases of Al, Si, Fe, Cu, Zn, As, Sr, Ag, Cd, In, Sn, Sb, Te, Ba, Au, Hg, Tl, Pb and Bi. He further connects the lines of greater wave-length with the substance *a*; and, as in all cases so far tried all the lines can be deduced from these two substances, he is led to believe that *all the so-called elements are compounds of the primary elements a and b.*

It is unfortunate that Dr. Grünwald has not published a complete list of the lines characteristic of *a* and *b*, for until this is done his theory cannot be accurately tested. There are two distinct questions to be answered: (1) Are there any numerical relations connecting the spectra of the elements? and if so, (2) What is the meaning of the fact? Cornu, Deslandres and others have long since answered the first question for us, but whether Dr. Grünwald's answer to the second one is correct or not depends upon the completeness with which the numerical relations hold for the *entire* spectra of the substances. It is here that Dr. Grünwald's work can be criticised.

As noted above, the spectrum of the oxyhydrogen flame is used to test the existence of lines belonging to *a* and *b*. By far the most accurate and complete determination of this spectrum is that of Liveing and Dewar (Phil. Trans. 1888); but this does not always answer Dr. Grünwald's purposes. In the B. A. report for 1886 there is a provisional list of lines of the water-spectrum, which he often uses, although the wave-lengths have since been corrected. Further, if other lines are necessary, they are found by halving the wave-lengths of the secondary spectrum of hydrogen. Many lines thus determined are actually present in the water-spectrum; but why are not *all* there? Dr. Grünwald says it is because the amplitude of vibration of parts of the molecule can be so changed, owing to the presence of other substances, that the intensity may increase or diminish, or become too faint to be observed. To this argument there is absolutely no answer. In some cases, too, the average of two wave-lengths is used as a criterion of a wave-length of *b* which falls between them! And as a last resort, if the necessary wave-length cannot be found in the water-spectrum by any of these means, it is put down as "new" and is called an "unobserved" line. As just shown, Dr. Grünwald easily explains why the strongest lines in the spectrum of an element, cadmium for example, when "transformed" into water-lines, may be faint; and *vice versa.* But how does he account for the fact that double lines are not transformed into double lines? This seems to me a fundamental objection. The concave-grating gives the only accurate method of determining the ultra-violet wave-lengths of the elements; and, as a consequence of not using it, most of the tables of wave-lengths so far published are not of much value. So Grünwald's error here may be great. And, besides, when we consider that in the water spectrum as given by Liveing and Dewar, without the help of the secondary spectrum of hydrogen, there is on the average one line for every two Angström units, it would be remarkable indeed if any law could not be verified. This is strikingly shown in the first group of the cadmium lines. Here 6742 and 6740 are two readings for the wave-lengths of the *same* line, as made by two observers; yet Grünwald finds a water-line for each of them!

The fact that there are exact numerical relations connecting the spectra of different elements does not afford a proof of Grünwald's hypothesis; and, until the above difficulties are removed, the evidence is against it. But, even granting it, how do we know that *a* and *b* are not themselves compounds? In the "second group" of cadmium lines there are 19 lines which can be transformed into *b* lines; *b* has many other lines; so at the most this shows only that cadmium and *b* have a common constituent, unless, of course, the absence of the other cadmium lines is accounted for in Grünwald's own way of varying intensity.

The lines of the spectrum of any one substance, as carbon or iron, seem to fall into definite series or groups; and the wave-lengths of the lines in these groups can be expressed by formulas, as is well known. All that the fact of there being a connection between the spectra of different substances seems to show is, then, that there may be a formula common to many elements, as Kayser and Runge have recently found. And all that this means is that the molecules of these elements vibrate in general according to a similar law.

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NOTES.

Boric Acid.

As is well known, in any family of base-forming or positive elements, the positive character grows less marked as the atomic weight decreases. Considering the position of boron in the periodic system, at the head of the aluminium family, and considering, further, the fact that aluminium hydroxide is a weak base, we should expect to find that the corresponding hydroxide of boron has but slight basic properties. That it is not entirely devoid of basic properties is shown by the existence of the phosphate, BPO_4; the sulphate, $B_2(SO_4)_3.H_2O$; and a compound analogous to tartar-emetic in which boron takes the place of antimony.

A strong argument in favor of the view that boron and aluminium are closely related elements is found in the isomorphism of euclasite and datholite. The analogy in composition between these minerals is shown by the formulas:

$2BeO.Al_2O_3.2SiO_2.H_2O$ . . . . Euclasite
$2CaO.B_2O_3.2SiO_2.H_2O$ . . . . . Datholite.

Attention has recently been called to the facts above-mentioned by P. Georgievic, who is engaged upon an investigation of boric acid, particularly with reference to the relative strength of the acid. He also calls attention to the following points:

1. Solutions of alkali carbonates and bicarbonates are not changed by boric acid. Although this fact has long been known to those engaged in the manufacture of borax, it is not mentioned in any text-book of chemistry.

2. A solution of borax absorbs such large quantities of carbon dioxide when this gas is conducted into it, that the boric acid is in all probability entirely replaced. Further, barium borate suspended in water is completely dissolved in a few minutes by passing hydrogen sulphide through the liquid.

3. When boric acid is added to a solution of potassium iodide and iodate, or of potassium iodide and nitrite, not a trace of iodine is set free.

4. The dark red color produced by adding ferric chloride to a solution of an acetate does not disappear on adding boric acid. The same is true of the purple color caused by bringing phenol and ferric acetate together.

Finally, the author suggests that the avidity of boric acid as given by Ostwald, viz., 0.01, is probably too high, for the reason that acetic acid, to which is ascribed the avidity 0.03, has the power to set iodine free when applied as directed under 3 above; and, further, when an acetate is used and boric acid added, iodine is not set free.—(*Journal für praktische Chemie* 38, 118.) I. R.

Hydrazine.

In the course of investigations on the diazo- and azo-compounds of the fatty series, Th. Curtius and J. Lang[1] have shown that when the ethyl salt of diazo-acetic acid, $CHN_2.CO_2C_2H_5$, is treated with a concentrated aqueous solution of caustic alkali, a salt of triazo-acetic acid, $C_3H_3N_6(COOH)_3$, is formed. This acid is stable in the free condition, and when boiled with mineral acids it gives up its nitrogen in the form of hydrazine, N_2H_4. The main reaction involved is that represented in the equation:

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[1] J. prak. Chem. [2] **38**, 521.

$$C_3H_3N_6(COOH)_3 + 6H_2O = 3C_2O_4H_2 + 3N_2H_4.$$

The oxalic acid which is the other product of the reaction is, however, more or less completely transformed into carbon dioxide and formic acid, a fact which is expressed in this equation:

$$C_3H_3N_6(COOH)_3 + 6H_2O = 3CO_2 + 3HCOOH + 3N_2H_4.$$

Hydrazine is formed also by the following reactions:

1. By reduction of ethyl diazo-acetate by zinc-dust and acetic acid,[1] or by aluminium or zinc filings in alkaline solution; and

2. By boiling with water the addition-products which the ethereal salts of diazo-acetic acid form with the ethereal salts of unsaturated acids.

The decomposition of triazo-acetic acid is, however, by far the best method for preparing hydrazine. The yield is about 90 per cent. of the theoretical.

Th. Curtius and R. Jay[2] have made hydrazine and its derivatives the subject of an extensive investigation, the results of which are briefly summarised in this note. As regards the quantities with which they worked, an experiment is described in which they treated 245 grams of triazo-acetic acid in 2 liters of water with 300 grams of pure concentrated sulphuric acid. On cooling, pure hydrazine sulphate was deposited in colorless crystals. On evaporating the mother-liquor, a second deposit of the sulphate was obtained. From the last mother-liquors the remaining hydrazine was extracted by shaking with benzoic aldehyde, with which it forms an insoluble compound of the formula $N_2(CH.C_6H_5)_2$, called benzalazine. From benzalazine the hydrazine is then obtained by treating with sulphuric or hydrochloric acid:

$$(C_6H_5CH)_2N_2 + 2H_2O + H_2SO_4 = 2C_6H_5CHO + N_2H_4.H_2SO_4.$$

Hydrazine combines with one or two molecules of monobasic acids to form stable salts. Even in acid solution these have extraordinary reducing power, the products of the action being nitrogen and water. When heated alone they decompose at a high temperature, forming ammonium salts, nitrogen and hydrogen. When a nitrite is added to hydrazine salts, nitrogen is rapidly evolved. Of the salts thus far examined, only the sulphate is difficultly soluble in water. The salts are either insoluble or but slightly soluble in alcohol. Some of them crystallise very well, and most of them appear to be isomorphous with the corresponding ammonium salts. The physical properties of hydrazine itself are as yet unknown. It appears from what has thus far been learned that it is a gas or a liquid boiling at a low temperature. That its molecular weight is correctly represented by the formula N_2H_4 follows from the existence of the two hydrochloric acid salts, $N_2H_4.HCl$ and $N_2H_4.2HCl$, and also from the results obtained in determining the molecular weight of benzalazine by Raoult's method. The compound has a remarkable affinity for water, and forms a hydrate of the composition $N_2H_4 + H_2O$. As, in setting hydrazine free from its salts it is necessary to use the oxides or hydroxides of the alkali metals or of the metals of the alkaline earths, and as water is necessarily formed in the reaction, thus:

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[1] J. prak. Chem. [2] **38**, 440.

[2] Ibid. [2] **39**, 27.

$$N_2H_4(AH)_2 + M_2O = N_2H_4 + H_2O + 2MA,$$

it follows that hydrazine is always obtained in the form of the hydrate. An attempt was made to break up this hydrate by distilling a mixture of hydrazine dichloride and quicklime from a silver vessel, and passing the volatile product through a silver tube filled with pieces of quicklime. No gas was obtained, and only a small quantity of a liquid came over. This proved to be hydrazine hydrate. It was shown further that barium oxide has not the power to decompose hydrazine hydrate into water and hydrazine. A large quantity of the hydrate has been made by distilling the sulphate with potassium hydroxide from silver vessels, and fractioning the distillate. Details in regard to this remarkable compound will be given in a later article by Curtius and Schulz. Meanwhile the following is all that is said concerning it. It has the composition $N_2H_4 + H_2O$, and forms a colorless, inodorous liquid with a high refracting power, which fumes in the air and boils without change at 119°. Pure hydrazine hydrate does not change in closed vessels. At the boiling temperature it attacks glass strongly, and destroys cork and rubber. It has an alkaline taste, and leaves upon the tongue a burning sensation. It is an extremely active poison for lower organisms.

Hydrazine is the strongest reducing agent known. A neutral solution of platinic chloride is reduced to metallic platinum, which separates in beautiful pieces having a silver luster, or in the form of a mirror. In acid solution, on the other hand, platinic chloride is reduced only to platinous chloride. In the same way hydrazine hydrate precipitates all easily reducible metals in the cold. Silver separates in compact lustrous pieces, apparently of crystalline structure. With very dilute solutions most perfect mirrors of great beauty are obtained. From aluminium the hydroxide is precipitated; and chromic hydroxide is precipitated from solutions of chromates. With mercuric chloride there is first formed a yellow-colored double salt, from which metallic mercury soon separates. In acid solution ferric chloride is reduced to ferrous chloride, and cupric to cuprous chloride. Dropped upon mercuric oxide or quinone, hydrazine hydrate causes an explosion. The facts mentioned show that this substance is undoubtedly destined to play an extraordinarily important part in analytical chemistry, and extensive investigations are now in progress with reference to its applications in this field. I. R.

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Contributions from the Chemical Laboratory of Harvard College.

LXIII.—ON SODIC ZINCATES.

By Arthur M. Comey and C. Loring Jackson.

Although the solubility of zincic hydrate in alkalies is one of the most familiar facts in chemistry, very few attempts, so far as we can find, have been made to determine what compounds exist in such a solution. The reason for this is not far to seek, as the results obtained by the few who have studied this subject are so decidedly unsatisfactory that they are not likely to induce others to take up this line of work.

The first important papers in this field appeared in the *Annalen der Chemie und Pharmacie* in 1834, having been brought out by a prize offered from the Hagen-Bucholz foundation for work on zincic oxide. Of the various competitors, Laux,[1] who was most successful in his work on this part of the subject, found that a solution of zincic oxide in caustic alkali, if covered with a layer of alcohol, gradually deposited little shining crystals, which were easily soluble in water, and, he states, contained equal molecules of zincic oxide and the alkaline oxide (ZnO_2K_2). These crystals were decomposed by heat, giving a white powder, which contained one molecule of alkaline oxide to two of zincic oxide; but no analyses of either of these substances are given.

Two other competitors for this Hagen-Bucholz prize, Bonnet[2] and Sander,[3] also touch on this subject, but their results are of less importance. Sander, in fact, comes to the conclusion that no definite compound is formed when zincic oxide is dissolved in a caustic alkali.

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[1] Ann. Chem. (Liebig) **9**, 183.

[2] Ibid. **9**, 177.

[3] Ibid. **9**, 181.

The next paper on the subject was published in 1842, by Fremy,[1] who states that the compounds formed by zincic oxide and an alkali were in general deliquescent and amorphous, but by using a potassic hydrate solution of zincic oxide, and adding to it a small quantity of alcohol, long needles were obtained, which he considered a "bi-zincate of potassa." It was immediately decomposed by water into zincic oxide and potassic hydrate. A few years later, in his article in the *Annales de Chimie et de Physique*,[2] Fremy states that he has met with great difficulties in obtaining the crystals, and hopes to return to the subject when he has determined the conditions under which they are formed. Neither of his papers contains analyses, and he has never published anything more on the subject, the reason for which we can well understand after our unsuccessful attempts to prepare potassic zincates.

The work on the ammonic zincates has led to about the same unsatisfactory results, no analyses of laboratory products having been published; but Malaguti[3] gives an analysis of an incrustation found upon a brick in the vault of a privy, which had the composition $3ZnO.4NH_3.12H_2O$.

The only other research which has approached this subject is one by Prescott,[4] published in 1880, on the solubility of zincic oxide in caustic alkalies. He found that more alkali is needed for complete solution of the zincic oxide than would be required by the following reaction,

$$ZnSO_4 + 4KOH = Zn(OK)_2 + K_2SO_4 + 2H_2O,$$

but this excess was smaller in the case of sodic or ammonic hydrate than with potassic hydrate; also that the excess of alkali could be neutralised in such a solution without precipitating zincic hydrate, until the amount was reached indicated by the reaction given above. Addition of a large quantity of water precipitated the zincic hydrate from the solution, even when it contained the excess of alkali. The effect of dilution and temperature on the solubility was also studied, but the determination of the composition of the substances formed did not come within the scheme of his work.

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[1] Comptes Rendus **15**, 1106.

[2] Ann. chim. phys., Ser. **12**.

[3] Comptes Rendus **62**, 413.

[4] Chem. News **42**, 30.

As, therefore, we could find in the chemical literature no analyses of a zincate, with the exception of Malaguti's ammonic zincate, we decided to take up the subject, and fortunately began our work with the sodic zincate, since this proved to be the one of them all which can be most easily prepared.

The principal results which we have obtained can be briefly summarised as follows: From a solution of zincic oxide in aqueous sodic hydrate, two crystalline sodic zincates can be separated by the action of alcohol; the principal product, which fuses below 100°, has the formula $Zn_3O_6Na_4H_2.17H_2O$; the other, which does not fuse at 300°, is $(ZnO_2NaH)_2.7H_2O$. Both substances are decomposed into zincic oxide and sodic hydrate by water or alcohol. We had hoped at first to extend our work to other zincates, but, after a number of experiments, have abandoned this intention, as with potassic hydrate no crystalline or definite compound could be obtained, and although ammonic hydrate gave a product crystallising in needles, it was obtained with difficulty, and proved to be of varying composition. We give, however, at the end of this paper, a brief account of the negative results of these experiments, and of some others in similar directions.

Preparation of the Sodic Zincates.

The sodic zincates can be prepared by the action of sodic hydrate on either metallic zinc, zincic oxide, or zincic hydrate, and the product seemed to be the same in every case. It is most convenient, therefore, to prepare them from zincic oxide, as the metallic zinc dissolves very slowly, long boiling with aqueous sodic hydrate being necessary to prepare a sufficiently strong solution. On the other hand, we have not succeeded in preparing the sodic zincates from sodic carbonate, as a mixture of this substance with zincic oxide showed no loss of weight even when kept at a white heat for some time. The method adopted by us consisted in dissolving zincic oxide in a strong aqueous solution of sodic hydrate,[1] with the aid of heat, in a flask, which was usually closed with a cork fitted with a set of potash bulbs, to prevent the absorption of carbonic dioxide by the alkaline liquid, but this precaution was not absolutely necessary. The solution, after it had cooled, was treated with twice or three times its volume of alcohol, and the mixture, after being thoroughly shaken, allowed to stand securely corked for about twenty-four hours. During this standing two layers were formed, a heavy aqueous solution and a lighter alcoholic liquid. These were separated, the aqueous solution treated again with alcohol in the same way, and this extraction with alcohol repeated until the heavier portion solidified shortly after it had been removed from the alcohol, which happened usually after the third or fourth extraction. The crystalline mass thus obtained we have called fusible sodic zincate, because it melts below 100°. The second sodic zincate was obtained from the alcoholic washings, which were mixed, and allowed to stand in a corked flask, when after some time, which varied from a few hours to several days, white crystals were deposited on the sides of the flask, which gradually increased in quantity. The formation of these crystals did not occur invariably, but they could often be made to appear by adding more alcohol to the washings. This compound deposited from the alcoholic washings does not fuse even at 300°, and we shall call it infusible sodic zincate.

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[1] The sodic hydrate used by us had been purified by alcohol.

Analysis of the Fusible Sodic Zincate, $Zn_3O_6Na_4H_2.17H_2O$.

This substance is the principal product of the reaction, forming, as nearly as we could estimate, over 90 per cent. of the total product. Since both water and alcohol decompose it, a further purification seemed impossible, and we were obliged to analyse it as it was obtained by the precipitation with alcohol, simply drying it by pressure between filter paper under heavy weights.

The method of analysis, which we adopted after trying several others, consisted in dissolving the substance in dilute sulphuric acid, and precipitating the zinc by means of a measured quantity of a standard solution of sodic carbonate. The zinc was weighed as oxide. The filtrate was acidified with sulphuric acid, evaporated to dryness, weighed, and then the amount of sodium calculated after subtracting from the total weight of the sodic sulphate the weight of sodic sulphate corresponding to the sodic carbonate added.

I. 0.4720 gram of the substance gave 0.1744 gram of zincic oxide and 0.2080 gram of sodic sulphate.

II. 0.6420 gram of the substance gave 0.2302 gram of zincic oxide and 0.2718 gram of sodic sulphate. 0.8802 gram of substance from the same preparation lost at 240° 0.3920 gram of water, and the dried product gave, on heating with chromic oxide in a stream of dry oxygen, 0.0342 gram of water.

III. 0.9682 gram of the substance gave 0.3370 gram of zincic oxide and 0.3992 gram of sodic sulphate. 0.8770 gram of substance from the same preparation lost at 240° 0.4021 gram of water.

	I.	II.	III.
Zinc,	29.66	28.78	27.93
Sodium,	14.28	13.72	13.36
Water,	...	44.54	45.83
Constitutional Water,	...	3.88	...

Each of these three analyses was made with a sample from an entirely separate preparation, in order to determine whether the substance had a definite composition, and when it is remembered that it could not be purified by crystallisation, and was dried only imperfectly by pressing with filter paper, the agreement is as close as could be expected; but it is obvious that in a case like this the atomic ratios are of much more importance than the percentages, and we have accordingly calculated them as follows:

Atomic Ratio of Zinc to Sodium in Fusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.	:	1.36
II.	1.	:	1.35
III.	1.	:	1.35

The agreement between these numbers proves conclusively that the substance is a definite compound, and that the proportion of zinc to sodium is as three to four. In trying to calculate a formula for it, we have felt much doubt in regard to the amount of water of crystallisation, for the reasons given above; but the one finally adopted by us gives percentages which agree so well with those found that it cannot be far from the truth, especially as the amounts of water found are about as much higher than those calculated as was to be expected. The constitutional water, on the other hand, comes very high, but we do not have much faith in this determination.

	Calculated for $Zn_3O_6Na_4H_2.17H_2O$.	Found		
		I.	II.	III.
Zinc,	28.28	29.66	28.78	27.93
Sodium,	13.30	14.28	13.72	13.36
Water,	44.24	...	44.54	45.83
Constitutional Water,	2.60	...	3.88	...

To prove that the substance contained water, and not alcohol of crystallisation, a combustion of it was made in the usual manner, but only a mere trace of carbonic dioxide was obtained.

The formula of this substance, $Zn_3O_6Na_4H_2.17H_2O$, agrees, except in water of crystallisation, with that of the substance analysed by Malaguti (see page 146), which, written in the same way, becomes $Zn_3O_6(NH_4)_4H_2.9H_2O$. This, as has been mentioned already, is the only zincate of which an analysis has been published.

We have made only one analysis of another preparation of this substance which is comparable to those given above; this gave about the same percentage of zinc, 29.45, but a much larger amount of sodium, 19.56, which was undoubtedly due to a small quantity of sodic hydrate left adhering to the crystals, as this was the first preparation we made, and therefore was not pressed out so thoroughly as the later ones, after we had become more familiar with the manipulation.

Properties of the Fusible Sodic Zincate.

The substance as precipitated by alcohol from its solution in aqueous sodic hydrate forms a white mass, made of radiating crystals, often of considerable size. It fuses at about 70°, but, owing to the difficulty of drying it, no attempts were made to determine the melting point accurately. Water decomposes it rapidly and completely, converting it into a white insoluble powder, which gave on analysis the following result:

0.1990 gram of the substance gave 0.1910 gram of zinc oxide and no sodic sulphate.

	Calculated for		
	ZnO_2H_2.	ZnO.	Found.
Zinc,	65.72	80.28	77.03

The substance therefore seems to be principally zincic oxide mixed with a slight impurity of the hydrate. Alcohol decomposes it in a similar way, but more slowly, as is shown by the following percentages obtained from the analyses of two preparations (IV, V), which we had attempted to purify by washing with alcohol:

	III.	IV.	V.
Zinc,	27.93	29.96	33.36
Sodium,	13.36	12.27	10.48

III is one of the analyses already given. The substance for this analysis was only pressed with filter paper. IV was a sample which had been washed three times with common alcohol, while the substance which had the composition given under V had been washed four times with absolute alcohol. These numbers show that the action of the alcohol consists in gradually removing the sodium as sodic hydrate, and this point is brought out even more sharply by a comparison of the atomic ratios.

	Zinc	:	Sodium.
III.	1.	:	1.35
IV.	1.	:	1.16
V.	1.	:	0.89

It follows from what has been said on this subject that care must be taken not to continue longer than is absolutely necessary the treatment with alcohol during the preparation of the sodic zincate. Although the substance is decomposed by both alcohol and water, it seems to exist during the process of manufacture dissolved in a mixture of these solvents in presence of an excess of sodic hydrate, an observation which is confirmed by that of Prescott (see page 146). It is insoluble in ether, and absorbs carbonic dioxide rapidly from the air. At 100° it loses only 12 molecules of its water of crystallisation, as is shown by the following analysis:

0.4720 gram of the substance analysed under I, when heated to 100° in a stream of pure dry air, lost 0.1510 gram of water.

	Calculated for a loss of $12H_2O$.	Found.
Water,	31.23	32.00

Analyses and Properties of the Infusible Sodic Zincate, $(ZnO_2NaH)_2.7H_2O$.

This substance, which crystallises from the alcoholic washings obtained in the preparation of the fusible compound just described, is formed in comparatively small quantities. As nearly as we could estimate, only a few per cent. of the total product consisted of it. As, like the fusible compound, it is decomposed by both water and alcohol, no attempt was made to purify it further, but it was analysed after drying at ordinary temperatures by the method already described (see page 148).

I. 0.7470 gram of the substance gave 0.3424 gram of zincic oxide and 0.2913 gram of sodic sulphate; 0.4762 gram of substance from the same preparation lost at 220° 0.1637 gram of water.

II. 0.6044 gram of the substance lost at 300° 0.2066 gram of water, and gave 0.2700 gram of zincic oxide and 0.2355 gram of sodic sulphate.

	Calculated for $(ZnO_2NaH)_2.7H_2O$.	Found. I.	II.
Zinc,	35.32	36.78	35.86
Sodium,	12.50	12.62	12.62
Water,	34.24	34.37	34.19

The considerable difference between the percentages of zinc is not greater than was to be expected, when the impossibility of purifying the substance is remembered. Each of these analyses was made with a sample from a separate preparation, and we add the following analysis, made early in the work simply to determine the ratio between the zinc and sodium, no care having been taken to dry the substance.

III. 0.7025 gram of slightly moist substance gave 0.2260 gram of zincic oxide and 0.1951 gram of sodic sulphate.

The percentages derived from this analysis are of course of no value, but it gives an atomic ratio which agrees with those from the preceding analyses so closely that there can be no doubt that this substance possesses a definite composition.

Atomic Ratio of Zinc to Sodium in the Infusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.03	:	1.
II.	1.03	:	1.
III.	1.02	:	1.

A combustion of the substance showed that it contained no alcohol.

This substance undoubtedly corresponds to the crystalline body obtained by Fremy (see page 146), who assigned to it the same ratio between the zinc and potassium. Laux (see page 145), on the other hand, ascribed to his crystals, which were soluble in water, the formula ZnO_2K_2, but stated that upon heating these crystals he obtained an amorphous powder which showed the ratio of 1 : 1 between zinc and potassium; that is, the same obtained in the crystals by Fremy and us. We have met with no substance corresponding to the soluble crystals of Laux.

Properties.—The infusible sodic zincate crystallises from a solution in dilute alcohol containing an excess of sodic hydrate in white needles, sometimes over a centimeter long, forming loose radiating groups usually of a conical shape, but occasionally circular or spherical. It does not melt even at 300°, and is decomposed by alcohol, or water, if these solvents are free from sodic hydrate, absorbs carbonic dioxide from the air, but much less rapidly than the fusible compound, and does not lose the whole of its water of crystallisation until heated above 200°.

We have not succeeded in finding any other definite compound among the products of the action of sodic hydrate on zincic oxide, and if any other exists, it can be only in very small quantity.

After we had settled the composition of the sodic zincates, we turned our attention to the study of other zincates, and also tried some experiments with magnesic oxide. The results of all this work were negative, but nevertheless we think it best to give a brief statement of what we have done.

In all our attempts to prepare potassic zincate we encountered the difficulties already mentioned by Fremy; in fact, we have not succeeded in obtaining in any experiment the crystals described by him, although we have modified the process employed in a number of different ways; but the solution of zincic oxide in potassic hydrate, when treated with alcohol according to the method which had yielded such good results with sodic zincate, gave only amorphous precipitates, which looked like zincic oxide, but were not wholly free from potassium; as the absence of crystalline form left us no means by which we could judge of the purity of this substance, we did not think it worth analysis.

With ammonic hydrate the results looked more promising at first, as the solution of zincic hydrate in ammonic hydrate occasionally gave a small quantity of crystals, after it had been mixed with alcohol and allowed to stand; but in this case there was no separation of the liquid into two layers. These crystals looked very much like the infusible sodic zincate described above, but the analyses of four preparations showed that they had no constant composition, the following percentages being obtained:

	I.	II.	III.	IV.
Zinc,	48.66	45.90	...	59.96
Ammonia,	7.35	4.58	3.67	5.28

In view of these results it did not seem worth while to continue the investigation.

In beginning this research we had hoped, by acting on the sodic zincate with a cobaltous salt, to obtain Rinman's green, and in this way throw some light on the composition of this pigment. These hopes have not been fulfilled, as the zincates were decomposed by alcohol or water, as already stated, and therefore the action could not be carried on in solution, and the melted fusible zincate, when treated with cobaltous chloride, gave only a blackish precipitate with no shade of green. The same result was obtained when an ethereal or absolute alcohol solution of cobaltous chloride was allowed to act on the zincate. We have also made many attempts to purify Rinman's green, prepared according to the usual method, in order to fit it for analysis, but none of these have succeeded, the substance being decomposed by solutions of alkalies or acids, in fact even by a solution of carbonic dioxide under pressure, which dissolved both zincic and cobaltous carbonates, and finally left a blackish gray residue.

Although magnesic hydrate does not dissolve in sodic hydrate under ordinary conditions, we thought that possibly a very strong solution of sodic hydrate might have some solvent action at its boiling point, and upon trying the experiment, obtained long prismatic crystals, which, however, we found contained only a mere trace of magnesium (0.39 per cent.), and consisted of the crystallised sodic hydrate recently obtained by Cripps,[1] as shown by the following analytical results:

I. 0.5620 gram of the substance lost 0.2150 gram of water.

II. 0.4115 gram of the substance gave 0.4585 gram of sodic sulphate.

	Calculated for $(NaOH)_3.4H_2O$.	Found.	
		I.	II.
Water,	37.50	38.26	...
Sodium,	35.93	...	36.11

The curious point about this observation, which alone makes it worth recording, is that the solution of sodic hydrate used could not be made to crystallise before it was treated with magnesic oxide, but after such treatment crystallised so rapidly that it was impossible to filter it. The experiment was repeated several times, each time with the same result. What the cause of this difference in behavior may be we have been unable to determine, but think that possibly a small quantity of sodic carbonate in our solution of sodic hydrate may have prevented the crystallisation, which took place as soon as this was converted into hydrate by the magnesic oxide.

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[1] Pharm. Jour. Trans., Ser. 3, **14**, 833 (1884).

ON THE ATOMIC WEIGHT OF OXYGEN.

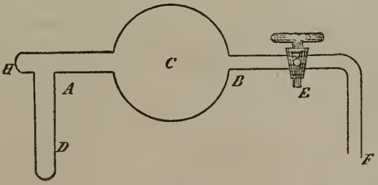
By W. A. Noyes.

The great importance which attaches to the atomic weight of oxygen makes it very desirable that this constant should be determined by several methods and by independent workers.

The method to be described was suggested to the author of this paper when reading Keiser's first paper.[1] A somewhat similar method has been proposed for a different purpose by Morley.[2]

The results which I have thus far obtained I consider as only preliminary, and they are presented now because it is necessary to discontinue the work for some time, and because they may be of some interest to others who are working in the same field.

The fundamental idea of the method is that by passing hydrogen into an apparatus containing hot copper oxide, and condensing the water formed within the same apparatus, the weight of the hydrogen can be determined by the gain in weight of the apparatus. The form of apparatus which was found best suited for the purpose is illustrated in the accompanying cut. It was made by Emil Greiner in New York.



C is a bulb with a capacity of 30 to 50 cc. and will contain 90 to 150 grams of copper oxide. The tube *H* was open when the apparatus was received from the maker. A small plug of asbestos was first placed at *B*, the bulb *C* was filled with carefully ignited copper oxide (Kahlbaum's best in wire form), and the tube was sealed at *H*. The volume of the apparatus was then determined by weighing in air and in water, and a counterpoise of nearly the same volume and of somewhat less weight was prepared. The tube *F* was then connected with a Sprengel pump by means of a bulb containing phosphorus pentoxide, and the air was pumped out. During the exhaustion the bulb was heated in an appropriate air-bath. After exhaustion, the apparatus was allowed to cool and was then weighed, using the counterpoise before mentioned. The balance used was made by Ruprecht in Vienna, and the weight of the apparatus (150 to 220 grams) could easily be determined to $\frac{1}{10}$ milligram. The apparatus was always allowed to stand in the closed balance-case for several hours, and usually over night, before the weight was finally determined. The volume of the counterpoise and weights was the same as that of the apparatus, within 1.5 cc. in every case, and usually somewhat closer. The greatest difference of temperature between the two weighings which gave the hydrogen was four degrees, and the greatest difference in pressure was seven millimeters. Supposing the differences to have occurred at the same time and in the same direction, and the difference in volume to have been 1.5 cc., the error from this source would have been four one-hundredths of a milligram.

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[1] Ber. d. chem. Ges. **20**, 2323.

[2] This Journal **10**, 22.

No correction to vacuum was necessary, as all of the weights for a determination were made with an apparatus of the same volume, and were determined with weights whose relative values had been determined by calibration *in the air.*

After weighing, the apparatus was again placed in the air-bath and heated while it was connected with an apparatus giving carefully purified hydrogen. The connection at *F* was sometimes made with a short piece of rubber tubing, the two tubes being brought together within it and the whole covered with mercury to prevent possible leakage or diffusion, and sometimes by a ground glass joint lubricated with a little grease. Each method seemed to serve equally well, except in one case, when a little mercury was drawn in through the rubber joint. In that case a low result was obtained, probably because of the vapor of mercury taken up by the hydrogen. When the hydrogen is first admitted to the apparatus through the three-way cock, it rushes over the copper oxide, and only a part of it is converted into water. Very soon a condition is reached when the side-tube *D* is filled with hydrogen, while the bulb is filled with nearly pure water-vapor. The hydrogen slowly diffuses back to the copper oxide, where it is converted into water-vapor, while the water-vapor diffuses into *D* and is condensed. The tube *A* and the opening into *D* are made about one cm. in diameter, that the diffusion may be as rapid as possible. *D* is cooled by immersion into distilled water. From two to four liters of hydrogen can be passed into the apparatus and converted into water in an hour. In a part of the experiments, the results of which are given below, a U-tube was used in place of the bulb to contain the copper oxide, but that form of apparatus was found less suitable.

After passing in a suitable amount of hydrogen, the stop-cock was closed, and by continuing the heating for a short time, all of the *gaseous* hydrogen was converted into water. The apparatus was then cooled and weighed with the same precautions as at first. The apparatus was then connected with a Sprengel pump by means of a bulb surrounded with ice-water. After exhausting the bulb and the tube *F*, the stop-cock was turned, and the small amount of nitrogen which always remained in the apparatus was pumped out and delivered into a eudiometer, where it was measured and further examined. Meanwhile the tube was heated in the air-bath, and the tube *D* was surrounded with hot water. As the water in *D* had been for several hours in an almost perfect vacuum, the water on the outside could be heated to boiling without fear of any ebullition within the tube. The water evaporated quite rapidly from the surface, and 6 or 8 cc. could be expelled from the apparatus in about an hour. In some of the experiments the apparatus was then connected with a vacuous bulb filled with phosphorus pentoxide, while in others it was cooled and weighed without this step. The vapor remaining in the apparatus in the latter case was very small in amount, and was determined along with the water obtained by reoxidising the reduced copper. After cooling and weighing, the apparatus was again placed in the air-bath and heated, and oxygen from a gasometer was passed in. The oxygen was passed over heated copper oxide, through a strong solution of caustic potash, and over stick potash and phosphorus pentoxide.

At this point arose one of the most serious questions with regard to the process. It was found that, even after very prolonged heating in pure oxygen, the copper would not take up as much oxygen as had been taken from it by the hydrogen. The explanation seems to be that the hydrogen, as it reduces the copper oxide, leaves the copper in a porous condition, so that the last traces of oxygen can be taken from it by the hydrogen. When the oxygen is passed in, however, the copper on the surface is oxidised first and the copper oxide formed, filling a greater volume than the copper; the pores are almost or quite closed, and the copper within is protected from further oxidation. Whether the copper loses all of the hydrogen which it has absorbed, as Keiser has shown that palladium does, is, perhaps, a question. The only direct evidence which has been thus far obtained on this point was one case in which the copper was heated twice in an atmosphere of oxygen. On the first heating it absorbed two grams of oxygen and gave 0.0160 gram water. On thes econd heating the copper absorbed one-half gram of oxygen and gave only 0.0013 gram water. The heating in the second case was continued for two hours. In other cases the heating was continued much longer, and the reoxidation was still far from complete. Even in some cases when copper reduced in hydrogen and reoxidised in oxygen was used, the copper could not, after a second reduction, be made to take up the same amount of oxygen again. If the copper remaining unoxidised still retained hydrogen, it would seem that the determinations of Cooke and of Keiser must have been subject to an error from the same source. Such an error must have been very small, but it is desirable that some determinations should be made by means of another agent than copper oxide.

After passing in the oxygen, the apparatus was cooled and weighed. It was then heated again, and the gases remaining in it pumped out into a eudiometer, while the water formed was received in a bulb filled with phosphorus pentoxide. On cooling and weighing, the loss of weight, less the weight of the gases pumped out, as determined by analysis, gave the weight of water obtained from the hydrogen which had been absorbed by the copper. Errors in any of these last weights would have only one-ninth as great an effect on the result as errors in the weights by which the amount of the hydrogen was determined. The amount of the water obtained after the oxidation of the copper was quite variable, partly because in some cases the bulb was only connected with the vacuous bulb surrounded with ice-water before reoxidation and so remained filled with aqueous vapor at a very low tension, and partly because the copper oxide used had been reduced and only partly reoxidised as stated above, and in such cases the amount of metallic copper was much greater in proportion to the amount of water fisrt formed than in other cases.

The hydrogen was prepared from pure (?) zinc and pure hydrochloric acid. The latter was of specific gravity 1.12, and was boiled carefully and partly cooled in a current of hydrogen before it was introduced into the flask from which it was fed to the generator. Also, pieces of pure zinc were put into it, to more thoroughly wash out dissolved gases and to furnish nascent hydrogen which should remove the last traces of oxygen from the liquid. Contact with the air was carefully avoided, and the acid was fed into the generator from a flask filled above with hydrogen, either by an arrangement similar to that described by Cooke, or with hydrogen from an independent generator. After the introduction of the hydrochloric acid into the feed-flask, a solution of blue chromous chloride was added. This was obtained by the reduction of potassium pyrochromate with zinc and hydrochloric acid. Its purpose was to absorb any traces of oxygen, and to give evidence of any air in the apparatus, by its change in color. The heavy flask used for a generator had a capacity of one liter, and had but one neck. The rubber stopper, bearing four tubes, was sunk into the neck, and covered with a thin layer of mercury, to prevent possible diffusion. The acid was fed by a siphon, and only its vapor came in contact with the stoppers. When hydrogen from the generator was used in the feed-flask, the stopper of the latter was surrounded with a jacket filled with mercury.

From the generator the hydrogen was passed through a 20-bulb tube filled with a 30 per cent. solution of caustic potash, to which some lead chloride was added. The latter revealed the presence of a small amount of hydrogen sulphide. Next was an 8-bulb tube containing a 3 per cent. solution of potassium permanganate, then a layer of hot copper. This was omitted in the first determinations, and was introduced from fear of a trace of oxygen from the potassium permanganate. After its introduction, a trace of hydrogen sulphide was found in the strong caustic potash solution which followed. This may have come from the rubber joints at both ends of the tube containing the copper. These joints could not be sealed, as they were between hard and soft glass. The joint at the other end of the potassium permanganate tube was also of rubber, because the solution required frequent renewal. The tubes were brought close together within these joints, and they were covered with jackets filled with water, to prevent diffusion. All other joints were made by fusing the glass together. After the copper, the hydrogen passed a strong caustic potash solution, to which lead sulphate was added in the later experiments, and then over stick potash and over phosphorus pentoxide mixed with asbestos. Glass-wool was avoided, because a specimen examined was found to have so low a specific gravity as to prove that it consisted—in part, at least—of fine glass tubes, and it was feared that the air in these would diffuse out slowly and mix with the hydrogen. After passing the phosphorus pentoxide an overflow tube was provided, dipping under mercury.

In calculating the results, the weight of the hydrogen, determined by the gain in weight of the apparatus, was corrected by subtracting the weight of the gas which was obtained in removing the water formed, as described above. This gas was calculated as nitrogen. In every case but one, however, oxygen was added in excess, then hydrogen, and the mixture was exploded. The results would seem to indicate that the gas contained from six to eleven thousandths of a milligram of hydrogen, but it is believed that this apparent result came from the formation of a small amount of oxides of nitrogen by the explosion. The oxygen was determined by the loss in weight of the apparatus after the water was removed. To this was added eight-ninths of the weight of the water obtained by reoxidising the copper.

Two determinations are omitted in the results given below. In one of these, mercury leaked by the rubber joint, and some of its vapor probably entered with the hydrogen. In the other, a small amount only of the hydrogen was used, and the accidental error was probably large. The other determinations were as follows:

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by reoxidation.	Corrected hydrogen.	Corrected oxygen.	Per cent. of oxygen reabsorbed.	Atomic weight.
1.	0.9449	7.4785	0.0006	0.0215	0.9443	7.4976	31	15.880
2.	0.6760	5.3521	0.0016	0.0034	0.6744	5.3551	28	15.881
3.	0.7879	6.2432	0.0013	0.0137	0.7866	6.2554	43	15.905
4.	0.5527	4.3483	0.0006	0.0420	0.5521	4.3856	61	15.887
5.	0.4278	3.3366	0.0004	0.0631	0.4274	3.3927	65	15.876
6.	0.8271	6.5437	0.0006	0.0249	0.8265	6.5658	27	15.888

Mean = 15.886 ± .0028

It is of special interest to compare this result with that obtained by Cooke, who prepared his hydrogen from the same materials. His result was 15.869, and the probable error of his first series is one half greater than that of this series, while that of his second series is but little less than this. *If the correction for nitrogen is omitted, the mean of these determinations becomes* 15.867, *or almost exactly the same as Cooke's final mean.* It seems to the author that the evidence is almost conclusive that Cooke's hydrogen was contaminated with a trace of nitrogen. While the amount of nitrogen can be rendered very small (in one case less than ½ cc. in ten and one-half liters), it would seem to be impossible to entirely exclude it with such generators as Cooke and myself have used.

In this series, the apparatus for purifying the hydrogen and also the condition of the copper oxide were repeatedly varied, in the endeavor to discover sources of constant error. One determination has also been made, using dilute sulphuric acid instead of hydrochloric. The result was 15.874.

The results obtained show that the accidental errors of the determination have been made very small. When the result is compared with that obtained by Keiser, however, I am inclined to believe that there must be in these determinations, as well as in those of Cooke, some source of constant error which has not yet been discovered.

ROSE POLYTECHNIC INSTITUTE, *Dec.* 15, 1888.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.

VI.

BY W. A. NOYES AND W. B. WILEY.

Oxidation of Para-nitro-ortho-toluene-sulphamide.

In previous papers[1] it has been shown that when ortho-sulphamides are oxidised with potassium ferricyanide, ortho-sulphamine-benzoic acids are obtained. Fahlberg[2] has shown that some of these acids may also be obtained by oxidation with potassium manganate and by boiling sulphinides with a solution of caustic potash, or by evaporating to dryness with the latter.

The first oxidations of the nitro-toluene sulphamide were made with potassium ferricyanide, as described in previous papers, and the ortho-sulphamine acid was obtained as expected. Some oxidations were also made with potassium manganate prepared by the directions of Fahlberg,[1] and also with an alkaline solution of potassium manganate, prepared by partially reducing a strongly alkaline solution of potassium permanganate with alcohol. An attempt was also made to obtain the acid by boiling the potassium salt of the corresponding sulphinide with a three per cent. solution of caustic potash. The sulphamine acid seems to be formed in this way, but its formation is accompanied by a deeper-seated decomposition, and the products obtained were difficult to separate. The most satisfactory method of those tried was to boil the sulphamide with a strongly alkaline solution of potassium permanganate. 30 grams of caustic potash and 8 grams of potassium permanganate were dissolved in about 150 cc. of water, and the solution was heated to boiling by passing steam into it. 5 grams of the amide were then added and the solution shaken vigorously. The oxidation took place rapidly and the permanganate was reduced in a few minutes. A three per cent. solution of potassium permanganate was then added in small portions and the solution was heated with steam. As soon as the solution remained green for several minutes after the addition of a new portion of the permanganate, the last portions of the manganate were reduced with alcohol, the solution was filtered, the filtrate was very nearly neutralised with hydrochloric acid and was evaporated to a small bulk. The solution was then made strongly acid and was extracted with ether. The acid remaining after distilling the ether was converted into the barium salt, the solution of the latter was evaporated to dryness and treated repeatedly with alcohol to remove a small amount of the unoxidised amide. The salt was then crystallised from water, and from the crystallised salt the acid was separated by means of hydrochloric acid. After filtering off, it was recrystallised from water.

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[1] This Journal **8**, 176, and **9**, 93.

[2] Ber. d. chem. Ges. **21**, 243.

Para-nitro-ortho-sulphamine-benzoic Acid.

The acid separates, on cooling its hot solution, in small granular crystals which are almost white. These melt at 172° if heated quickly. If heated more slowly they melt at 177°, but if kept for a short time at that temperature they are converted into the sulphinide, and, after solidifying, melt at 209°. The acid is easily soluble in alcohol, quite easily soluble in ether, and rather difficultly soluble in water.

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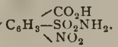
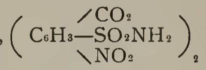
[1] Loc. cit.

I. 0.1052 gram of the acid gave 0.1002 gram $BaSO_4$.

II. 0.1015 gram of the acid gave 0.0959 gram $BaSO_4$.

	Calculated for  $C_6H_3\begin{cases}CO_2H\\SO_2NH_2\\NO_2\end{cases}$.	Found. I.	II.
S	13.01	13.09	12.99

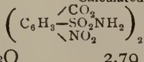
Barium Nitro-sulphamine-benzoate,  $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2 Ba + H_2O$.—This was obtained and purified as described above. The salt may also be crystallised from alcohol. It separates from the solution in hot alcohol, on cooling, in fine feathery needles. These contain one molecule of water. The salt crystallised from water contains a larger amount of water, but loses a part of it easily on air-drying, and when dried over sulphuric acid appears to contain but one molecule of water. The analyses, however, are not very accordant. The salt loses its water at 105°, but after being dehydrated at that temperature, the same amount of water is quickly regained on exposure to the air. When heated to 135° the salt loses weight slowly, and is, apparently, converted into the salt of the corresponding sulphinide. At a higher temperature the loss in weight indicates that the conversion is quantitative. The salt of the sulphinide loses its water easily at 105°. Analysis II, below, was with a salt crystallised from alcohol. The other analyses were with salts crystallised from water. All but the first were dried over sulphuric acid.

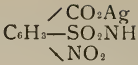
I. 0.2021 gram of the salt gave 0.0719 gram $BaSO_4$.

II. 0.2066 gram of the salt lost 0.0049 gram H_2O at 105° and gave 0.0736 gram $BaSO_4$.

III. 0.1403 gram of the salt lost 0.0037 gram H_2O at 105° and gave 0.0496 gram $BaSO_4$.

IV. 0.3230 gram of the salt lost 0.0121 gram H_2O at 105° and gave 0.1161 gram $BaSO_4$.

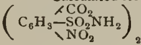
	Calculated for  $\left(C_6H_3\begin{cases}CO_2\\SO_2NH_2\\NO_2\end{cases}\right)_2 Ba + H_2O$.	Found. I.	II.	III.	IV.
H_2O	2.79	...	2.37	2.64	3.83
Ba	21.24	20.90	20.93	20.77	21.12

Silver Nitro-sulphamine-benzoate,  $C_6H_3\left\{\begin{array}{l}CO_2Ag\\SO_2NH_2\\NO_2\end{array}\right. + \frac{1}{2}H_2O.$ — This was prepared by adding silver nitrate to the hot solution of the barium salt. On cooling, the salt separated in short, thick needles of a light yellow color. The salt loses nothing over sulphuric acid, and loses water but slowly at 105°.

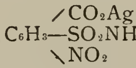
I. 0.1070 gram of the salt gave 0.0317 gram Ag.

II. 0.1167 gram of the salt lost 0.0020 gram H_2O at 135° and gave 0.0348 gram Ag.

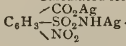
III. 0.1221 gram of the salt lost 0.0028 gram H_2O at 135° and gave 0.0365 gram Ag.



	Calculated for $\left(C_6H_3\left\{\begin{array}{l}CO_2\\SO_2NH_2\\NO_2\end{array}\right.\right)_2 + \frac{1}{2}H_2O.$	Found. I.	II.	III.
$\frac{1}{2}H_2O$	2.49	...	1.71	2.29
Ag	29.83	29.63	29.82	29.89

Di-silver Nitro-sulphamine-benzoate,  $C_6H_3\left\{\begin{array}{l}CO_2Ag\\SO_2NHAg\\NO_2\end{array}\right. + H_2O.$ —This salt was prepared by adding a very small amount of ammonia to the mother-liquors of the last salt. It separated at first as an amorphous precipitate which passed into solution on heating. After filtering and cooling, the salt separated as a greenish yellow crystalline powder. It loses one-half its water at 105°, the remainder at 135°.

0.0577 gram of the salt lost 0.0022 gram H_2O at 135° and gave 0.0260 gram Ag.



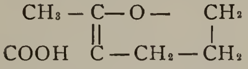
	Calculated for $C_6H_3\left\{\begin{array}{l}CO_2Ag\\SO_2NHAg\\NO_2\end{array}\right. + H_2O.$	Found.
H_2O	3.76	3.81
Ag	45.19	45.06

ROSE POLYTECHNIC INSTITUTE, *Dec.* 17, 1888.

SOME DERIVATIVES OF HEXA-METHYLENE.

By Paul C. Freer and W. H. Perkin, Jr.[1]

The substance previously described as methyl-dehydrohexone-carboxylic acid,



when boiled with water, yields aceto-butyl alcohol,

$$CH_3.CO.CH_2.CH_2.CH_2.CH_2OH.$$

This substance, when treated with sodium amalgam, is easily converted into δ-hexylene-glycol,

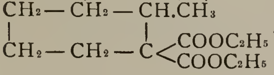
$$CH_3.CHOH.CH_2.CH_2.CH_2.CH_2OH.$$

If this glycol be digested with concentrated aqueous hydrogen bromide, the corresponding methyl-penta-methylene dibromide results,

$$CH_3.CHBr.CH_2.CH_2.CH_2.CH_2.Br.$$

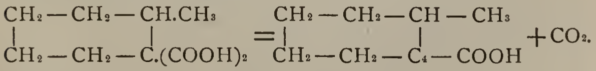
By the action of the sodium compound of malonic ether on this dibromide, hexa-methylene derivatives can be obtained, according to the following equation:

$$2CHNa(COOC_2H_5)_2 + CH_3.CHBr.CH_2.CH_2.CH_2.CH_2Br =$$



$$+ CH_2(COOC_2H_5)_2 + 2NaBr.$$

The resulting substance has been called ethylic methyl-hexa-methylene dicarboxylate (2.1.1.). This ether on saponification yields free methyl-hexa-methylene dicarboxylic acid, which latter, when distilled, decomposes into the corresponding mono-carboxylic acid and carbonic anhydride:



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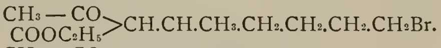
[1] Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 53, p. 202. Communicated by the authors.

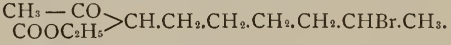
Ethylic methyl-hexa-methylene dicarboxylate is a thick, colorless oil, of disagreeable odor, boiling between 260°–265°, at 250 mm. pressure. The yield of this substance is not very satisfactory, owing to the formation of a considerable quantity of a higher boiling substance, the constitution of which will be explained in a future paper. The dicarboxylic acid obtained from this ether by means of saponification with alcoholic potash, is a sandy, crystalline powder, melting at 147°, with partial decomposition into the mono-carboxylic acid and carbonic anhydride. It is readily soluble in ether, alcohol, and hot water, more sparingly soluble in cold water. Methyl-hexa-methylene mono-carboxylic acid is a thick, colorless oil, of a most penetrating and disagreeable odor. It boils at 235°–236°. Its physical properties agree closely with the formula assigned to it.

In carrying out this investigation it was thought that interesting results could be obtained by studying the action of methyl-penta-methylene dibromide on the sodium derivative of aceto-acetic ether; as in this case it was doubtful whether hexa-methylene derivatives, or compounds containing a carbon-oxygen ring, would result. In the case of the action of tri-methylene bromide on sodium aceto-acetate, it will be remembered, a body belonging to the latter class was exclusively produced.

If one molecular proportion of sodium aceto-acetic ether be digested with one of methyl-penta-methylene dibromide, a substance $C_{12}H_{21}O_3Br$ is produced. This may have either of the following formulae:

(1) 

$$\left.\begin{matrix}CH_3-CO\\COOC_2H_5\end{matrix}\right>CH.CH.CH_3.CH_2.CH_2.CH_2.CH_2Br.$$

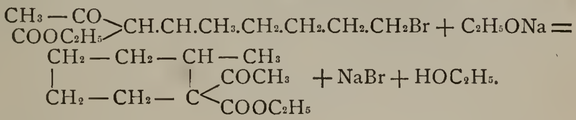
(2) 

$$\left.\begin{matrix}CH_3-CO\\COOC_2H_5\end{matrix}\right>CH.CH_2.CH_2.CH_2.CH_2.CHBr.CH_3.$$

Which of these is correct we cannot state, and, as the constitution of the substance subsequently obtained is not affected thereby, we have not attempted to distinguish between them.

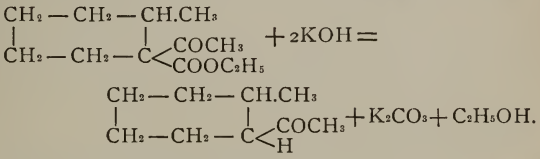
If this bromine compound is treated with zinc-dust and acetic acid, the bromine atom is readily replaced by hydrogen. To determine the constitution of the above compound it would, therefore, only be necessary to compare this reduction-product with hexyl-aceto-acetic ether. If the substance be identical with this latter, formula 2 would be correct; if isomeric, formula 1 must be assigned to it.

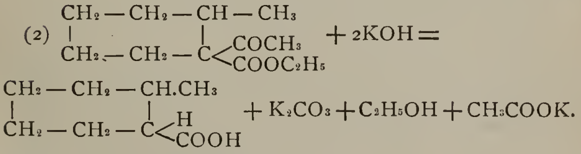
The bromine compound $C_{12}H_{21}BrO_3$, when treated with sodic ethylate, or the sodium compound of aceto-acetic ether, is converted into ethylic acetyl-methyl-hexa-methylene carboxylate,



That the substance so produced is really a hexa-methylene derivative is shown by a study of its decomposition-products resulting from saponification. When boiled with alcoholic potash it is easily decomposed, with formation of methyl-hexa-methylene-methyl ketone and methyl-hexa-methylene carboxylic acid, thus:

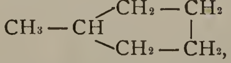
(1)





The methyl-hexa-methylene carboxylic acid obtained in this manner was identical with that obtained by the action of methyl-penta-methylene dibromide on the sodium compound of malonic ether.

If methyl-penta-methylene dibromide be dissolved in ether, and granulated sodium then gradually added, violent reaction sets in; the bromine atoms are entirely eliminated, and a hydrocarbon remains after evaporating the ether. This hydrocarbon gives numbers on analysis which agree with the formula,



which is that of a substance which could be called methyl-penta-methylene. The hydrocarbon thus produced boils at 70°–71°, and seems to be isomeric with all of the hexylenes as yet known. It differs from these in the property of not being attacked by a concentrated aqueous solution of hydrogen iodide. Until a further study shall have fully proved its constitution, however, nothing definite can be said about it.

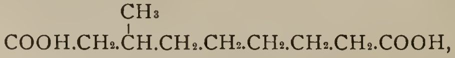
EXPERIMENTS ON THE SYNTHESIS OF HEPTA-METHYLENE DERIVATIVES.[1]

By Paul C. Freer and W. H. Perkin, Jr.

When malonic ether is treated with methyl-penta-methylene dibromide, two substances are produced. One of these has already been described in the paper on hexa-methylene derivatives; the other, which is formed in considerable quantity, is the product of the reaction of two molecules of malonic ether with one of the dibromide, thus:

$$2(COOC_2H_5)CHNa + CH_3CHBr(CH_2)_3CH_2Br = \\ (COOC_2H_5)_2CH.CH.CH_3.(CH_2)_4CH(COOC_2H_5)_2 + 2NaBr.$$

This ethereal salt, for which we propose the name ethylic isoheptane $(\omega_2\omega_2)$ tetracarboxylate, is a colorless oil, boiling at 273°–276° at 60 mm. pressure. This ethereal salt, on saponification, is easily converted into the corresponding acid, and this latter, when heated slowly in a metal bath to 200°, is decomposed into carbonic anhydride and a brownish-colored oil, which was purified by means of conversion into the corresponding ether. This ether is a colorless liquid of peculiar odor, boiling at 307°–308°, under ordinary pressure. The substance so produced is the ethereal salt of methyl-azelaic acid, $COOC_2H_5.CH_2.CH(CH_3).(CH_2)_5COOC_2H_5$. This, when saponified with a solution of caustic potash in methyl alcohol, yields pure methyl-azelaic acid,



$$COOH.CH_2.\overset{\overset{\displaystyle CH_3}{|}}{C}H.CH_2.CH_2.CH_2.CH_2.CH_2.COOH,$$

a white crystalline substance melting at 43°–44°, separating from solvents as an oil, which only solidifies after standing over sulphuric acid in a vacuum. It is fairly soluble in boiling water, easily so in benzene, ether, and alcohol. Methyl-azelaic acid is isomeric with sebacic acid (m. p. 197°) and heptyl-malonic acid (m. p. 97°–98°).

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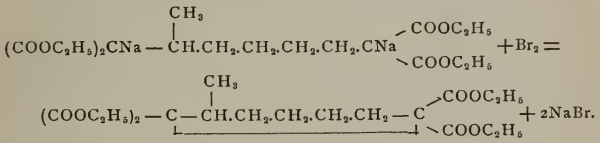
[1] Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 53, p. 215. Communicated by the authors.

When the ethereal salt of isoheptane-tetracarboxylate is treated with sodium-ethylate, a disodium compound is produced, owing to the fact that the substance contains two —CH— groups connected each with two carbethoxyles. This disodium compound, when suspended in a large quantity of dry ether, is readily acted on by bromine. This experiment was performed with the hope of effecting the synthesis of hepta-methylene derivatives, thus:



$$(COOC_2H_5)_2CNa-\overset{\displaystyle CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_2.CH_2.CNa\begin{matrix}\nearrow COOC_2H_5\\ \searrow COOC_2H_5\end{matrix}+Br_2=$$

$$(COOC_2H_5)_2-\underbrace{C-\overset{\displaystyle CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_2.CH_2-C}\begin{matrix}\nearrow COOC_2H_5\\ \searrow COOC_2H_5\end{matrix}+2NaBr.$$

It was found, however, that no hepta-methylene derivative resulted, for on saponification of the oil isolated from the ethereal solution, and subsequent decomposition into carbonic anhydride and an oily acid, this latter proved to be regenerated methyl-azelaic acid. As far as we could see, no other acid was produced. It is difficult to explain what takes place in a reaction of this kind; but one fact is very prominent — no hepta-methylene derivative results. The power of forming closed carbon chains seems to cease when the number of carbon atoms exceeds six.

Contributions from the Laboratory of the New York Agricultural Experiment Station.

IV.—ARTIFICIAL vs. ANIMAL DIGESTION.

By E. F. Ladd.

By means of the artificial digestion of feeding-stuffs, we can determine the relative digestibility for the albuminoids of the several substances, and the coefficients obtained serve as a measure of the digestibility of the fodder. That the coefficients obtained in artificial digestion correspond with the results obtained in actual digestion with animals is not claimed, but that they come quite close (although higher) to those figures may be shown by actual trials in comparison of artificial and animal digestion.

On four occasions, at the New York Agricultural Experiment Station, I have had an opportunity to test the value of artificial digestion as compared with animal digestion, and the results were in round numbers as follows for the albuminoids of the fodders:

	Pepsin digestion.	Animal digestion.
Corn fodder,[1]	54	49
Soja hispida,[1]	75	70
Orchard grass hay,[2]	62	60
Corn meal,[2]	64	58

We see by the above table that the coefficients obtained by artificial digestion for the albuminoids were invariably higher than the results secured with animals.

The digestibility of the albuminoids of corn meal as found in the trial was much lower than has heretofore been given. In this case the digestibility of the meal was determined with cows in ration of hay and corn meal, the digestibility of the hay having been previously determined separately with the same animals and *assumed* to be the same in the ration as when fed alone. It should be noted that the digestibility of corn meal as given, in most cases at least, has been made with hogs, animals very different in all respects from ruminants. With one exception, when a soft corn was used, I have never yet been able to obtain digestion coefficients for the albuminoids of corn meal as high as those given in the German tables, or as found by Jordon[3] in his trials with hogs, but the results given in the previous table for the pepsin digestion stand in about the same relation to animal digestion as in the trials with other feeds. Whether the digestion coefficients for the albuminoids of corn meal as now used are too high for ruminants, or whether in the trial I have reported[4] the digestibility for the albuminoids of the orchard grass hay was largely modified when compounded in a ration, remains to be determined by future investigations. That the digestibility was modified to some extent is probable, but not to the degree necessary to bring the figures for corn meal up to those usually given: and why this single anomaly in pepsin digestion?

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[1] This Journal 8, 434.

[2] Report of New York Agricultural Experiment Station, 1888; Proceedings of the Society for Promotion of Agricultural Science, 1888.

[3] Report of Maine Agricultural Experiment Station.

[4] Proceedings of the Society for the Promotion of Agricultural Science, 1888.

Taking the results of American digestion experiments and the average of my own for pepsin digestion on similar foods, we have the following parallels:

	Digestion Coefficients.	
	Pepsin.	Animal.
Timothy hay,	52	44
Clover hay,	57	53 to 56
Oat straw,	18	?
Maize fodder,	54	49 to 52

In the above table the figures given for both timothy and clover are the averages for twenty-one samples.

Stutzer, Jordon, and others have shown that the results obtained in animal digestion are below the actual amounts digested by the animals, due to the presence in the feces of biliary products, mucus matter, etc. The amount of the error depends upon the richness in albuminoids of the food under examination. Stutzer also thought that a portion of the albuminoids of feed-stuffs was indigestible, and this he called nuclein. This can hardly be true of all substances, and careful redigestion of several feeds leads us to think that in many fodders all of the albuminoids are in a digestible form. The following shows a few of our results for redigestion with pepsin:

	Per Cent. Albuminoids Digested.		
	First Trial.	Second Trial.	Third Trial.
Wheat,	79	34	29
Timothy hay,	59	29	34
Wheat bran,	77	23	11

How near to a complete digestion of the albuminoids might have been attained by drying the undigested residue, regrinding, and repeatedly digesting, I cannot say, but in each case a considerable quantity was digested in the third trial.

Stutzer, Jordon, and others have concluded from their investigations that if the animal feces are subjected to artificial digestion and the undigested portion taken as that undigested by the animal, then the difference between the total albuminoids and that which remains undigested by artificial digestion will be the real amount digested by the animal. I know of no proof to show that the pepsin solution does not digest from the feces some of the undigested portion of the food. That it may do this seems possible, from the facts already cited, and that, by redigesting the feces a second time, another portion of the albuminoids is digested, as shown below:

	Per Cent. Digested. No. 1.	No. 2.
First digestion,	18.13	13.10
Second digestion,	8.36	7.18

If we assume that the amount actually digested by the cow is the apparent amount plus that portion digested from the feces by a pepsin solution, then, instead of the digestion coefficient for the albuminoids of orchard grass hay being 60 per cent., it is nearly 68 per cent., or, if we take the amount redigested a second time, it will be considerably increased over the last figures.

From the data at our command we conclude:

1. That pepsin digestion furnishes us a reliable means of determining the digestibility of the albuminoids of our feeding-stuffs, and that this serves as a good criterion of the digestibility of the fodder itself.

2. That the coefficients of digestibility for albuminoids, as usually calculated from animal digestion, are too low.

3. That the digestibility of the albuminoids of corn meal, as given in the German tables, seems to be too high for ruminants.

4. That in many of our feeding-stuffs, all of the albuminoids seem to be in a digestible form.

5. That the digestion of the feces by a pepsin solution may, and probably does in most cases, give us results above what is actually digested by the animal.

GENEVA, N. Y., *September* 8, 1883.

Communications from the Chemical Laboratory of Rutgers College.

XVIII.—LECTURE-EXPERIMENTS WITH NITRIC ACID.

BY PETER T. AUSTEN.

Nitric acid, when in the state of a gas, makes an admirable subject for lecture-experiments. A number of experiments with the liquid form are given in Heumann[1] and other books on experimental chemistry, but the following experiments with the gaseous form I have not been able to find described. A flask can be filled with nitric acid gas by placing in it some strong pure nitric acid and boiling. This operation, however, takes some little time and is not always satisfactory, as the flask at first becomes filled with a mist. The better plan is to pour into a quart flask, having a neck wide enough to admit a deflagration-spoon, some commercial concentrated sulphuric acid in sufficient amount to cover the bottom of the flask about half an inch, and add to it ten to twenty grams of potassium nitrate. The potassium salt is better than the sodium salt, as it is less liable to contain nitrites, which will discolor the gas by the liberation of N_2O_3. The nitrate should be added in the form of crystals of about one-quarter of an inch in size. If added in a powdered condition, the mass cakes, and requires considerable shaking to disintegrate it. The coarser kind behaves admirably, and on heating the mixture the gas is liberated quickly and evenly.

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[1] Anleitung zum Experimentiren, p. 125.

The flask is hung free on a stand and a small naked flame applied. The nitric acid gas is liberated in large amounts and expels the air at once. This operation should be done under a hood, although, by regulating the heat carefully, it is easily possible to fill the flask and yet not drive off enough gas to cause discomfort. If the filling is done under a hood, the flask and stand are placed, when needed, on the lecture-table; heat, sufficient to prevent the condensation of the gas, being kept under the flask. The sulphuric acid solution on the bottom of the flask is practically invisible, and does not in any way interfere with the experiments.

Nitric acid acts in all of these experiments, except the last, as an oxidising agent, viz:

$$2HNO_3 = H_2O + N_2O_4 + O.$$

It will therefore serve as a source of oxygen, and its reduction will be indicated by the formation of the red N_2O_4. The strong color of this gas makes some of the experiments very striking. In fact, several of them are worthy of performance in the regular lecture-course. The temperature of the gas lies between 90°–100°. To get the full effect of the phenomena, the experiments should be performed in a partially darkened room, which, while permitting the details of the experiments to be observed, makes the combustions appear more brilliant.

Candle.—A lighted candle continues to burn, giving a brilliant flame surrounded by a large pale halo. The peroxide, N_2O_4, as in all of these experiments, forms at first in a large halo about the flame and eventually fills the flask. As this phenomenon occurs in every case, it will not be mentioned again. Owing to the heat of the gas, the candle melts rapidly. The dropping wax soon sets up an action with the mixture of sulphuric and nitric acids on the bottom of the flask. The experiment should be stopped before this begins.

Wood.—An ignited splinter of wood (a splinter fastened to an iron wire is best) burns energetically. A spark bursts into flame as in oxygen.

Charcoal burns brilliantly. If bark-charcoal is used, the scintillations in the red gas produce an unusually fine effect.

Steel Watch-spring.—The spring should be not over 1½ mm. wide and should be detempered. By winding sulphur-string about the end, igniting and introducing quickly, the steel soon ignites and continues to burn brilliantly, but with an effect quite different from the combustion in oxygen. In this case it is well to put a layer of sand half an inch deep in the flask, to prevent fracture of the bottom by the falling globules of fused iron.

Phosphorus burns with an intensely bright light as in oxygen. It soon volatilises and fills the flask with flame. Here again the tinging of the light by the red peroxide, N_2O_4, produces a peculiar effect.

Sodium takes fire without preliminary heating, and burns with an intense yellow light. A small piece and a deep spoon should be used, so as to avoid any chance of the melted sodium falling into the sulphuric acid, as such an occurrence is dangerous.

Magnesium when ignited burns with its characteristic white light.

Copper, *zinc* and *antimony* I have been unable to make burn.

Illuminating Gas.—A flame of gas, issuing from a bent-up glass tip, when inserted, continues to burn with a brilliant white center surrounded by a large red halo. At first the flame becomes musical, degenerates into a series of rapid, slight explosions, and is extinguished. The tone varies with the size of the flame. After a certain amount of peroxide, N_2O_4, is formed, the flame is not extinguished, and the musical tone also soon ceases.

Hydrogen sulphide burns with a bright, yellow flame. The flask becomes filled with thick vapors—probably a cloud of chamber-crystals arising from the action of the sulphur dioxide and water (which result from the combustion of the hydrogen sulphide) on the nitrogen tetroxide.

Hydrogen burns with an intensely white flame resembling the flame of illuminating gas just described. It does not become musical.

Caoutchouc.—A piece of black rubber tube, introduced in a deflagration-spoon, soon fuses and evolves gas, which ignites and burns with a large flame having a bright core and a pale halo. If the caoutchouc is ignited in the air, it burns with a white, smoky flame. When now introduced, the flame entirely loses its luminosity and becomes as described.

Turpentine boils violently and emits white fumes, which soon ignite with a gentle explosion and burn with a luminous flame.

Carbon disulphide does not ignite spontaneously, but when ignited and introduced, it continues to burn energetically. It soon volatilises and fills the whole flask with flame.

Benzene does not ignite spontaneously, but when ignited and introduced, it burns quietly with a white flame.

Ether evaporates and reduces the nitric acid gas to the tetroxide, N_2O_4. When ignited and introduced, it soon volatilises and fills the flask with luminous flame.

Hydrochloric Acid Gas.—A stream of the gas issuing from a turned-up tip did not react, nor could the gas be ignited by applying a flame at the point of mixture between the gases. Heating the tube through which the hydrochloric acid was delivered also failed to effect a decomposition.

Hydrobromic acid gas could not be made to react, although a slight decomposition occurred.

Hydriodic acid gas could not be made to ignite. On passing it into the nitric acid gas, however, decomposition and liberation of iodine gas took place. It is a difficult matter to regulate the evolution of hydriodic acid, so that my failure may have been caused by the irregularity of the pressure. Hofmann[1] has shown that drops of hot fuming nitric acid falling through an atmosphere of hydriodic acid produce a large red flame and deposition of iodine crystals. I shall make another attempt to ignite the gas, using a different form of apparatus.

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[1] Ber. d. chem. Gesell. **3**, 658.

Ammonia.—This experiment requires a little skill, but is not difficult. Ammonia is evolved in a six-ounce flask, by heating a mixture of ammonium chloride, slaked lime and water. The flask is clamped to a stand and heated with a small flame. The stopcock to this burner must be accessible without leaving the experiment, for by it is controlled the evolution of the ammonia gas. The success of the experiment depends on getting the right-sized jet of ammonia gas. The ammonia gas is led into the nitric acid gas by means of a glass jet, the tip of which turns up. This jet is connected with the evolution-flask by a sufficiently long rubber tube. The orifice of the jet should not be less than one-eighth of an inch in diameter; a small jet rapidly clogs and closes. The jet-tube should be about sixteen inches long, so that the rubber connection may not be attacked by the nitric acid gas issuing from the flask. The tube is grasped with a pair of tongs and lowered into the mouth of the flask. As the gases mix, a dense cloud of ammonium nitrate is produced. As soon as the jet is on a level with the mouth of the flask, it should be ignited by means of a wax gaslighter, and at the same instant the jet is lowered into the center of the flask. If the jet is of the right size and the pressure is neither too great nor too small, the ammonia will ignite easily and, on lowering into the flask, will continue to burn with a fine yellow flame. When once in position and burning evenly, the flame can be considerably enlarged by increasing the heat under the ammonia flask. The evolution must be regular, and to this end the flame under the ammonia flask should be protected against draughts.

The flame is a peculiar one, consisting of a yellow center, then a greenish-yellow envelope, and then a carmine-red envelope. As the color of the peroxide, N_2O_4, gets deeper, the flame becomes unusually handsome. The products of combustion are presumably oxides of nitrogen, perhaps free nitrogen, although I have not yet established this. It is a more striking experiment than the combustion of ammonia in a current of oxygen.

This experiment can be performed in a large oxygen globe. In this case the flask from which the ammonia is evolved must be provided with a trapped stand-tube filled with ammonia-water to give a pressure. In this way, or by using a large jet and carefully manipulating a clamp on the rubber supply-pipe, a large flame may be easily obtained.

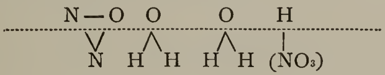
Nitric Oxide.—A jet of nitric oxide, N_2O_2, introduced into nitric acid gas reacts with it, the mixture turning at once red. The product of the reaction is probably nitrous acid,[1]

$$N_2O_2 + 2HNO_3 = 2HNO_2 + N_2O_4.$$

Nitrous Oxide.—A jet of moist nitrous oxide, prepared by heating ammonium nitrate, refuses to ignite in the nitric acid gas. I was surprised to observe, however, the formation of dense white clouds, which on examination proved to be ammonium nitrate. The reaction here is a synthesis of ammonium nitrate:

$$N_2O + 2H_2O + HNO_3 = NH_4NO_3 + HNO_3.$$

The molecule of nitric acid which appears on both sides of the equation is not an instance of chemical tautology, but is demanded, since the rest, NO_3, that appears in the new molecule of NH_4NO_3 is not derived from the $2H_2O$ and the N_2O, but from the HNO_3; for water and nitrous oxide do not unite at a moderate heat. If I interpret the mechanism of this reaction correctly, it should be represented by the following diagram:



ON PARA-NITRO-ORTHO-SULPHOBENZOIC ACID.[2]

By J. H. Kastle.

The investigation, the results of which are recorded in the following pages, was undertaken at the suggestion of Professor Remsen, and carried on under his guidance. The object in view was to throw light upon the chemical conduct of an acid in which the sulphuric acid residue and the carbonic acid residue are in the ortho relation to each other, the point of chief interest being a comparison of the acid with phthalic acid.

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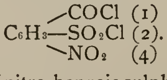
[1] Nitric oxide when led through concentrated nitric acid forms nitrous acid. Gmelin-Kraut, 6 ed. I, 2 Aufl. 454.

[2] From the author's dissertation for the degree of Doctor of Philosophy, at the Johns Hopkins University, 1888.

The constitution of phthalyl chloride has for some time been the subject of a good deal of discussion. In 1880 it was pointed out by von Gerichten[1] that the easy formation of phthalid from phthalyl chloride could be most easily explained by assuming that both chlorine atoms are in combination with one and the same carbon atom, and that the anhydride condition exists in phthalyl chloride just as it does in phthalic anhydride itself. At that time the strongest argument against this view was furnished by what was then held to be a fact, viz. that ethers obtained from this chloride by treatment with alcohol and phenol are identical with those obtained from phthalic acid itself. It remained for Graebe[2] to show that these ethers are not identical, as was formerly supposed, but really isomeric—the isomerism being most marked in the case of those obtained from tetrachlorphthalic acid.

In consequence of this, the above argument lost its weight, and since Graebe's investigation on the ethers of phthalic acid, the formula of von Gerichten for phthalyl chloride has been the one most generally accepted, although it must be said that there are still facts on record which speak against this view, particularly that of the formation of phthalimide from phthalyl chloride by the action of gaseous ammonia, a reaction which was found by Kuhara[3] to take place quantitatively, and which can easily be explained on the supposition that phthalyl chloride is made up in this way, $C_6H_4{<}\begin{smallmatrix}COCl\\COCl\end{smallmatrix}$, as was formerly supposed.

In view of all this, the action of phosphorus pentachloride on (*p*)-nitro-sulpho-benzoic acid has been carefully studied, and it has been found that the ethers produced by the action of different alcohols on the chloride thus obtained are not analogous to those obtained by Graebe in the case of phthalyl chloride, but are compounds of this order, $C_6H_3\begin{matrix}\diagup COOR\\ —SO_2OR\\ \diagdown NO_2\end{matrix}$; and consequently, in the chloride of (*p*)-nitro-sulpho-benzoic acid one chlorine atom is in combination with carbon, the other with sulphur, as represented in this formula,



$$C_6H_3\begin{matrix}\diagup COCl\ (1)\\ —SO_2Cl\ (2).\\ \diagdown NO_2\ \ (4)\end{matrix}$$

The easy formation of nitro-benzoic sulphinide from this chloride by treatment either with aqueous or gaseous ammonia also speaks strongly in favor of this view.

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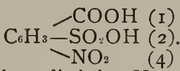
[1] Ber. d. chem. Gesell. **13**, 417.

[2] Ber. d. chem. Gesell. **16**, 860.

[3] This Journal **3**, 26.

The results obtained also show that (*p*)-nitro-sulpho-benzoic acid exhibits in a striking way the combined properties of both a sulphonic and a carbonic acid. And finally, from the study of the acid and its derivatives I have been led independently to the same view regarding the structure of the sulphinides as that first proposed by Remsen[1] in 1879, and shown to be correct by Fahlberg and Brackett in 1887.

Paranitro-sulpho-benzoic Acid,  $C_6H_3\begin{cases} COOH & (1) \\ SO_2OH & (2) \\ NO_2 & (4) \end{cases}$.—The salts of this acid were first made and studied by Hart,[2] and were obtained by oxidising the calcium salt of nitro-toluene-sulphonic acid with potassium permanganate. The yield obtained by following Hart's directions was so small that I endeavored to find a better method for effecting the oxidation.

It was found advantageous to use the potassium salt of paranitro-toluene-sulphonic acid instead of the calcium salt; and, after a large number of experiments, the following method was found to give the best results:

Ten parts by weight of the potassium salt of (*p*)-nitro-toluene-sulphonic acid, together with 3 parts by weight of potassium hydroxide, are dissolved in 500 parts of water; the balloon-flask containing this solution is then placed on the water-bath, and when it has acquired the temperature of the bath, 22 parts by weight of potassium permanganate are added, and the mixture heated until the color of the permanganate has entirely disappeared. The amber-colored liquid is then filtered from the manganese hydrate, and the dark brown residue thoroughly washed with hot water. The filtrate and washings are then neutralised with hydrochloric acid, and evaporated until the neutral potassium salt begins to crystallise out, when a small quantity of the solution is cooled. The whole of the solution is then allowed to cool, and strong hydrochloric acid added in excess, when the acid potassium salt of paranitro-sulpho-benzoic acid separates out in beautiful fine white needles.

The following results show the excellent yield which it is possible to obtain by following these directions:

1st experiment, 10 grams potassium *p*-nitro-toluene-sulphonate gave 9.5 grams acid potassium nitro-sulpho-benzoate; 2d experiment, 10 grams gave 9.4 grams; 3d experiment, 50 grams gave 48 grams; 4th experiment, 250 grams gave 240 grams.

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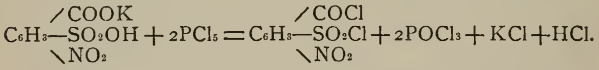
[1] This Journal **1**, 429.

[2] Ibid. **1**, 340.

When the barium salt of (*p*)-nitro-sulpho-benzoic acid is dissolved in water which has been acidulated with hydrochloric acid, and the barium precipitated by sulphuric acid, a solution of (*p*)-nitro-sulpho-benzoic acid is obtained. This, when evaporated to a small bulk and allowed to cool, yields crystals of the free acid. The acid is very readily soluble in hot water, much less so in cold, and separates from a hot concentrated solution on cooling in beautiful white needles. These melt at 110° C. to a jelly-like mass which does not become perfectly liquid until a considerably higher temperature is reached.

Action of Phosphorus Pentachloride on Acid Potassium (p)-nitro-sulpho-benzoate.

When the acid potassium salt of (*p*)-nitro-sulpho-benzoic acid is intimately mixed with a little more than an equal weight of phosphorus pentachloride, and the mixture heated on the oil-bath to 150° C., reaction takes place with the formation of an acid chloride; phosphorus oxychloride is also formed, and hydrochloric acid is given off—a reaction which is expressed by this equation:



$$C_6H_3\begin{array}{l}\diagup COOK\\ -SO_2OH\\ \diagdown NO_2\end{array} + 2PCl_5 = C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 2POCl_3 + KCl + HCl.$$

The phosphorus oxychloride is distilled off, and there remains in the flask an acid chloride of a wax-like consistency, together with a small quantity of potassium chloride. The acid chloride is then washed with water in order to remove the last traces of the oxychloride and the potassium chloride. It is then separated as completely as possible from the water by means of a separating funnel, and dried over sulphuric acid. Prepared in this way, it is a yellow, wax-like solid, which on long standing over sulphuric acid becomes somewhat granular and crystalline.

It is slightly soluble in petroleum ether, and very readily soluble in chloroform and anhydrous ether. From the latter solvent it crystallises in fine yellow needles or in flat plates which are somewhat elongated. These crystals become waxy on heating, and at 60° they melt to a clear liquid which, on cooling, solidifies. The chloride cannot be distilled; on heating to boiling it decomposes. A chlorine determination, made by dissolving the chloride in dilute caustic potash and precipitating with silver nitrate, gave the following results:

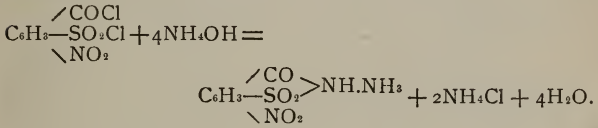
1.1956 grams of the chloride gave 1.1658 grams AgCl.

0.5089 gram of the chloride gave 0.5052 gram AgCl.

	Calculated for $C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl.\\ \diagdown NO_2\end{array}$	Found.
Cl	24.95 per cent.	24.11 per cent. 24.56 "

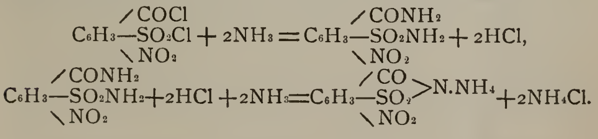
Action of Ammonia on the Chloride of (p)-nitro-sulpho-benzoic Acid.

When the chloride of (*p*)-nitro-sulpho-benzoic acid is treated with aqueous ammonia, a lively reaction takes place, and the ammonium salt of nitro-benzoic sulphinide is obtained. It is probable that the reaction takes place in this way:



$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 4NH_4OH = C_6H_3\begin{array}{l}\diagup CO\\ -SO_2\\ \diagdown NO_2\end{array}\!\!>NH.NH_3 + 2NH_4Cl + 4H_2O.$$

When the perfectly dry chloride is treated with dry ammonia gas, the ammonium salt of nitro-benzoic sulphinide is obtained, together with ammonium chloride; and the same result is reached by treating a solution of the chloride in anhydrous ether with gaseous ammonia. This reaction may be represented thus:

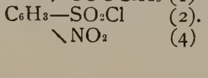


$$C_6H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 2NH_3 = C_6H_3\begin{array}{l}\diagup CONH_2\\ -SO_2NH_2\\ \diagdown NO_2\end{array} + 2HCl,$$

$$C_6H_3\begin{array}{l}\diagup CONH_2\\ -SO_2NH_2\\ \diagdown NO_2\end{array} + 2HCl + 2NH_3 = C_6H_3\begin{array}{l}\diagup CO\\ -SO_2\\ \diagdown NO_2\end{array}\!\!>N.NH_4 + 2NH_4Cl.$$

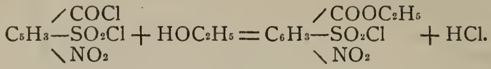
Action of Alcohols on the Chloride of (p)-nitro-sulpho-benzoic Acid.

The chloride of (*p*)-nitro-sulpho-benzoic acid dissolves readily in alcohol with a considerable evolution of heat, and from this solution, on cooling and standing for some time, there is deposited a quantity of white needle-shaped crystals, which were found to have the composition and structure represented by this formula,

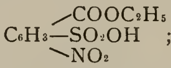


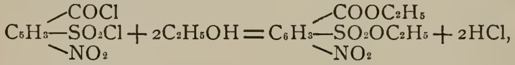
$$C_6H_3\begin{array}{ll}\diagup COOC_2H_5 & (1)\\ -SO_2Cl & (2).\\ \diagdown NO_2 & (4)\end{array}$$

Absolute alcohol acts on the chloride according to this equation,

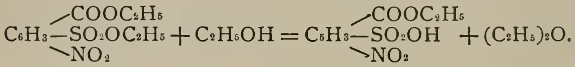


$$C_5H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + HOC_2H_5 = C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2Cl\\ \diagdown NO_2\end{array} + HCl.$$

When the chloride of (*p*)-nitro-sulpho-benzoic acid is boiled with absolute alcohol, another reaction takes place, and we have as the end-product of the reaction the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid,  $C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OH\\ \diagdown NO_2\end{array}$; and from certain studies which I have made on the saponification of the *mixed* ethers of (*p*)-nitro-sulpho-benzoic acid, it would seem that the formation of an acid ether from the chloride could be best represented by the following equations:

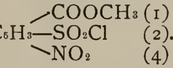


$$C_5H_3\begin{array}{l}\diagup COCl\\ -SO_2Cl\\ \diagdown NO_2\end{array} + 2C_2H_5OH = C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OC_2H_5\\ \diagdown NO_2\end{array} + 2HCl,$$



$$C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OC_2H_5\\ \diagdown NO_2\end{array} + C_2H_5OH = C_5H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OH\\ \diagdown NO_2\end{array} + (C_2H_5)_2O.$$

This reaction of the chloride of (*p*)-nitro-sulpho-benzoic acid with absolute alcohol has been found to be a general one, and it is only necessary to bring together this chloride with any primary alcohol to obtain the corresponding acid ether of (*p*)-nitro-sulpho-benzoic acid, or its acid chloride. As to which of these reactions will take place depends mainly on the temperature at which it is conducted.

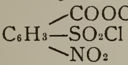
Chloride of the Acid Methyl Ether of (p)-nitro-sulpho-benzoic Acid,  $C_6H_3\begin{array}{ll}\diagup COOCH_3 & (1)\\ -SO_2Cl & (2)\\ \diagdown NO_2 & (4)\end{array}$.—When the chloride of (*p*)-nitro-sulpho-benzoic acid is dissolved in methyl alcohol and the solution kept cool, there separates out, after a time, a white crystalline compound; the addition of a small quantity of cold water facilitates the separation. This compound is insoluble in cold water, and is soluble in hot water with decomposition.

It is soluble to some extent in cold alcohol, quite readily so in boiling alcohol, from which it separates, on cooling, in fine white needles which melt at 90° C. When the alcoholic solution is boiled for a long time, the compound is decomposed, and there is found in the solution hydrochloric acid and the acid methyl ether of (*p*)-nitro-sulpho-benzoic acid.

The compound is easily soluble in anhydrous ether, from which it crystallises on slow evaporation in flat, transparent crystals of a prismatic habit. A determination of the chlorine, made by decomposing the compound in dilute alkali and precipitating with silver nitrate, gave the following result:

0.3692 gram of the chloride gave .1925 gram AgCl.

	Calculated for $C_6H_3{<}\begin{smallmatrix}COOCH_3\\SO_2Cl.\\NO_2\end{smallmatrix}$	Found.
Cl	12.70 per cent.	12.95 per cent.

Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid,  $C_6H_3{<}\begin{matrix}COOC_2H_5 & (1)\\ SO_2Cl & (2)\\ NO_2 & (4)\end{matrix}$.—This compound is obtained by dissolving the chloride of (*p*)-nitro-sulpho-benzoic acid in absolute alcohol, care being taken to keep the solution cool.

It separates out of the alcoholic solution on standing, but the separation is greatly hastened by the addition of a small quantity of water. This compound, like the corresponding methyl compound, is insoluble in cold water, and readily decomposed by boiling water; the products of the decomposition being hydrochloric acid and the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid.

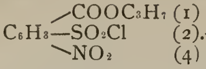
It is easily soluble in hot alcohol, from which it crystallises, on cooling, in fine white needles; it is also easily soluble in anhydrous ether, from which it crystallises, on slow evaporation, in large, well defined crystals of a prismatic habit. These are transparent and have a high lustre, and were found to belong to the monoclinic system. The substance melts at 67°–68° C. uncorrected, to a clear oily liquid which, on cooling, again solidifies.

The compound gave the following figures on analysis:

0.2471 gram of the chloride gave 0.1237 gram AgCl.

0.2419 gram of the chloride gave 0.1966 gram $BaSO_4$.

	Calculated for $C_6H_3{<}\begin{smallmatrix}COOC_2H_5\\SO_2Cl.\\NO_2\end{smallmatrix}$	Found.
S	10.90 per cent.	11.12 per cent.
Cl	12.09 "	12.30 "
N	4.77 "	4.41 " 4.70 "

Chloride of the Acid Propyl Ether of (p)-nitro-sulpho-benzoic Acid,  $C_6H_3\left\{\begin{matrix}COOC_3H_7 & (1)\\ SO_2Cl & (2)\\ NO_2 & (4)\end{matrix}\right.$.—About five grams of the chloride of (*p*)-nitro-sulpho-benzoic acid were dissolved in about 30 cc. of normal propyl alcohol, and the solution allowed to evaporate spontaneously. A substance crystallised out in white leaflets which was found to react in the same way as the ethyl compound just described. Although no analysis was made of this compound, there can be little doubt that it is made up in the manner represented above.

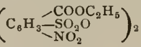
Action of Water on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

When this compound is boiled for some time with water it dissolves completely and an intensely acid liquid results. This acid solution was neutralised with barium carbonate, filtered, and the filtrate evaporated to one half its original bulk. On cooling, a barium salt crystallised out which was found to be identical in every way with the barium salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid (see p. 190).

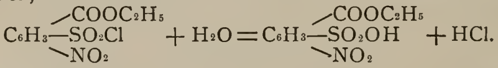
It gave the following figures on analysis :

0.2127 gram of the salt lost on heating to 150° 0.0203 gram.

0.1924 gram of the dried salt gave 0.0654 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3\left\{\begin{matrix}COOC_2H_5\\ SO_2O\\ NO_2\end{matrix}\right.\right)_2 Ba + 4H_2O$.	Found.
H_2O	9.51 per cent.	9.54 per cent.
	Calculated for the dried salt.	
Ba	20 per cent.	19.95 per cent.

The acid solution obtained in this experiment was also found to contain a considerable quantity of hydrochloric acid, and the action of the water on this compound can be best understood by this equation,



$$C_6H_3\left\{\begin{matrix}COOC_2H_5\\ SO_2Cl\\ NO_2\end{matrix}\right. + H_2O = C_6H_3\left\{\begin{matrix}COOC_2H_5\\ SO_2OH\\ NO_2\end{matrix}\right. + HCl.$$

Action of Alcoholic Ammonia on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

About five grams of the chloride were dissolved in about 50 cc. of a saturated alcoholic solution of ammonia ; the solution was then heated on the water-bath under pressure for about an hour.

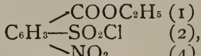
The solution thus obtained was evaporated on the water-bath, and the residue dissolved in hot water; on cooling, a substance crystallised out in thin leaflets having a sweet-bitter taste resembling that of nitro-benzoic sulphinide.

This substance was again dissolved in water, and a few drops of strong hydrochloric acid added, when a substance crystallised out in fine yellowish needles which were found to melt at 208°–209° C. uncorrected. In order to make sure that nitro-benzoic sulphinide had been formed in this experiment, the crystals melting at 208°–209° C. were dissolved in strong ammonia and reduced with sulphuretted hydrogen. The product of the reduction proved to be the amido-benzoic sulphinide, which was recognised by its intensely sweet taste, its fluorescent solution, and its melting point (284°–285° C.).

Action of Aqueous Ammonia on the Chloride.

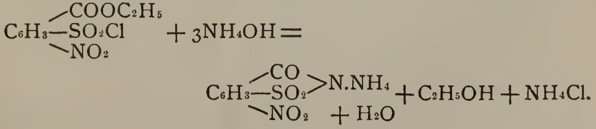
About 10 grams of the chloride were boiled with strong aqueous ammonia under a reflux condenser. When the chloride had completely dissolved, a portion of the liquid was distilled off. The distillate was neutralised with dilute sulphuric acid and redistilled. The distillate obtained was treated with dilute alkali and iodine, when a precipitate of iodoform was produced, thus proving that alcohol had been formed in the reaction.

The residue from the first distillation was found to contain the ammonium salt of nitro-benzoic sulphinide. This reaction is, I think, one of the strongest arguments in favor of the formula $R<\substack{CO\\SO_2}>NH$ as correctly representing the constitution of the sulphinides. It will be shown that the chloride of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid has, in all probability, the structure represented by this formula,

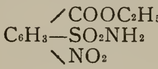


$$C_6H_3\begin{cases}COOC_2H_5 & (1)\\ SO_2Cl & (2)\\ NO_2 & (4)\end{cases}$$

and consequently the action of aqueous ammonia can be best explained by this equation,



$$C_6H_3\begin{cases}COOC_2H_5\\ SO_2Cl\\ NO_2\end{cases} + 3NH_4OH = C_6H_3\begin{cases}CO\\ SO_2\\ NO_2\end{cases}\!\!\!>N.NH_4 + C_2H_5OH + NH_4Cl. + H_2O$$

When perfectly dry ammonia gas is passed over the dry chloride which has been slightly warmed, quite a lively reaction takes place. Ammonium chloride is formed in considerable quantity, and on treating the mass which remains after the reaction with water, there is obtained, together with a large quantity of the ammonium salt of nitro-benzoic sulphinide, a small quantity of a substance which is soluble with difficulty even in hot water, and which crystallises from dilute alcohol in radial tufts of fine white needles. This substance melts at 141° C. uncorrected, and from its method of formation is probably to be represented by the formula  $C_6H_3{-}\begin{matrix}\nearrow COOC_2H_5\\ SO_2NH_2\\ \searrow NO_2\end{matrix}$, although it was not obtained in sufficient quantity for analysis.

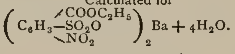
Action of Alcohol on the Chloride of the Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid.

A few grams of the chloride were heated with absolute alcohol in a pressure bottle in a water-bath, in the hope of obtaining the di-ethyl ether of (*p*)-nitro-sulpho-benzoic acid. After heating for about an hour, the resulting alcoholic solution was evaporated on the water-bath. Instead of obtaining a neutral ether, an intensely acid syrup was thus obtained, which became somewhat crystalline on cooling. This was dissolved in a large quantity of water and neutralised with barium carbonate. On concentrating the solution, a barium salt crystallised out in fine white needles having the appearance and properties of the barium salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid described on page 190.

It gave the following numbers on analysis :

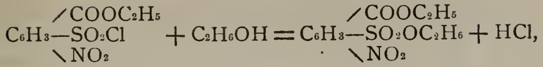
0.2714 gram of the salt lost on heating to 150° C. 0.0257 gram.

0.2457 gram of the dried salt gave 0.0841 gram $BaSO_4$.

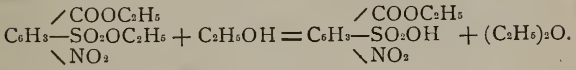


	Calculated for $\left(C_6H_3{-}\begin{matrix}\nearrow COOC_2H_5\\ SO_2O\\ \searrow NO_2\end{matrix}\right)_2 Ba + 4H_2O$.	Found.
H_2O	9.51 per cent.	9.47 per cent.
	Calculated for the dried salt.	
Ba	20 per cent.	20.10 per cent.

From a study of the saponification of the ethers of (*p*)-nitro-sulpho-benzoic acid, it seems highly probable that this reaction takes place thus :



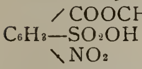
$$C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ —SO_2Cl\\ \diagdown NO_2\end{array} + C_2H_6OH = C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ —SO_2OC_2H_6\\ \diagdown NO_2\end{array} + HCl,$$



$$C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ —SO_2OC_2H_5\\ \diagdown NO_2\end{array} + C_2H_5OH = C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ —SO_2OH\\ \diagdown NO_2\end{array} + (C_2H_5)_2O.$$

ACID ETHERS OF (*p*)-NITRO-SULPHO-BENZOIC ACID AND SOME OF THEIR SALTS.

Acid Methyl Ether of (*p*)-*nitro-sulpho-benzoic Acid*,



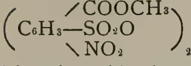
$$C_6H_3\begin{array}{l}\diagup COOCH_3\\ —SO_2OH\\ \diagdown NO_2\end{array}$$

.—When the chloride of (*p*)-nitro-sulpho-benzoic acid is dissolved in methyl alcohol, and this solution heated on the water-bath under an inverted condenser for about three hours, there separates out, on cooling, a quantity of beautiful fine white needles, which have a strong acid taste and reaction, and when dissolved in water the substance decomposes carbonates with ease.

The acid is difficultly soluble in methyl alcohol, very easily soluble in water, crystallising out of a very concentrated aqueous solution in fine white needles which show a strong tendency to concentric grouping. When heated, these crystals begin to blacken at 212°–215° C., and melt with decomposition at 270° C.

This acid forms stable, well defined salts, most of which have a strong crystallising power. The following salts have been made and studied:

Barium Methyl-(*p*)*-nitro-sulpho-benzoate*,

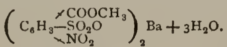


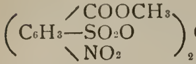
$$\left(C_6H_3\begin{array}{l}\diagup COOCH_3\\ —SO_2O\\ \diagdown NO_2\end{array}\right)_2 Ba + 3H_2O.$$

—This salt was made by neutralising the acid ether just described with barium carbonate. The salt crystallises in flat shining plates, or in yellow needles, and it is easily soluble in hot water; less soluble in cold.

The water of crystallisation and the barium were determined, with following results:

0.2103 gram of the salt lost on heating to 150° 0.0162 gram.
0.1941 gram of the dried salt gave 0.0689 gram $BaSO_4$.

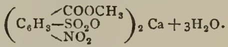
	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup COOCH_3\\ —SO_2O\\ \diagdown NO_2\end{array}\right)_2 Ba + 3H_2O.$	Found.
H_2O	7.59 per cent.	7.75 per cent.
	Calculated for the dried salt.	
Ba	20.85 per cent.	20.90 per cent.

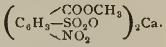
Calcium Methyl-(p)-nitro-sulpho-benzoate,  $\left(C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{array}\right)_2 Ca + 3H_2O$.—This salt was made by neutralising the free acid with precipitated chalk. The salt is very easily soluble in hot and cold water, and crystallises from a very concentrated solution in fine white needles which have a satiny lustre.

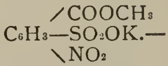
An analysis gave the following numbers:

0.2242 gram of the salt lost on heating to 140° 0.0182 gram.

0.2260 gram of the dry salt gave 0.0567 gram $CaSO_4$.

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{array}\right)_2 Ca + 3H_2O$.	Found.
H_2O	8.79 per cent.	8.11 per cent.

	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{array}\right)_2 Ca$.	Found.
Ca	7.14 per cent.	7.34 per cent.

Potassium Methyl-(p)-nitro-sulpho-benzoate,  $C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2OK\\ \diagdown NO_2\end{array}$.—This salt was made by neutralising the free acid with pure potassium carbonate. From a hot aqueous solution the salt separates out, on cooling, in beautiful white plates which show a beautiful iridescence, and resemble potassium chlorate in their general appearance. Under other conditions, however, when the salt has been allowed to crystallise slowly, it has been obtained in crystals of good size. Some of these crystals have been measured and studied by Mr. A. C. Gill.

The results of his measurements are as follows: The crystals are triclinic, having a perfect cleavage in the plane assumed as the base.

Five specimens having moderately good reflecting surfaces gave the following mean result: $\breve{a} : \bar{b} : c' = .6314 : 1 : .7104$. The angles between the pinacoids are as follows:

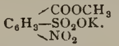
OP to $\infty P\bar{\infty}$, 58° 0′ 40″; OP to $\infty P\breve{\infty}$, 93° 27′ 30″; $\infty P\bar{\infty}$ to $\infty P\breve{\infty}$, 79° 20.

The development of the form P′ was very variable; on most of the crystals, especially the smaller ones, slight.

An analysis of the salt gave the following result:

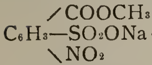
0.2208 gram of the salt lost on heating to 175° 0.0003 gram.

0.2205 gram of the dried salt gave 0.0645 gram K_2SO_4.



	Calculated for $C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2OK.\\ \diagdown NO_2\end{matrix}$	Found.
K	13.18 per cent.	13.10 per cent.

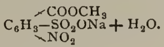
Sodium Methyl-(p)-nitro-sulpho-benzoate,



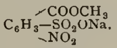
$C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2ONa\\ \diagdown NO_2\end{matrix} + H_2O$.—This salt was made from the calcium salt by treating a hot solution of the calcium salt with sodium carbonate. It is easily soluble in hot water, soluble with difficulty in the cold, and separates, when the hot solution is allowed to cool, in small white needles, sometimes in flat transparent plates.

0.2792 gram of the salt, when dried at 175°, lost 0.0142 gram.

0.2650 gram of the dried salt gave 0.0680 gram Na_2SO_4.

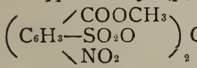


	Calculated for $C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2ONa + H_2O.\\ \diagdown NO_2\end{matrix}$	Found.
H_2O	5.98 per cent.	5.08 per cent.



	Calculated for $C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2ONa.\\ \diagdown NO_2\end{matrix}$	Found.
Na	8.12 per cent.	8.30 per cent.

Copper. Methyl-(p)-nitro-sulpho-benzoate,



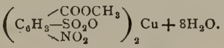
$\left(C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{matrix}\right)_2 Cu + 8H_2O$.—This salt was made by treating the barium salt with an equivalent amount of copper sulphate. The barium sulphate was filtered off and the green solution evaporated to a small bulk, when the copper salt crystallised out in thin leaflets showing a tendency to concentric grouping.

When perfectly dry the salt has a most beautiful apple-green color, together with a pearly lustre. It is easily soluble in hot and cold water. On being heated, the salt loses its water of crystallisation and becomes colorless.

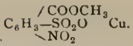
An analysis gives the following numbers:

0.2080 gram of the salt lost 0.0412 gram when dried at 180° C.

0.1668 gram of the dried salt gave 0.0177 gram Cu.



	Calculated for $\left(C_6H_3\begin{matrix}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{matrix}\right)_2 Cu + 8H_2O.$	Found.
H_2O	19.80 per cent.	19.80 per cent.

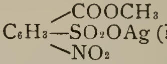


$$C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2O\\ \diagdown NO_2\end{array}Cu$$

	Calculated for $C_6H_3(COOCH_3)(SO_2O)(NO_2)Cu$.	
Cu	10.80 per cent.	10.61 per cent.

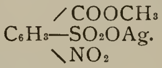
When a concentrated aqueous solution of the copper salt is treated with strong ammonia, a beautiful cupr-ammonium compound is formed which separates from the solution in dark blue needles.

Silver Methyl-(p)-nitro-sulpho-benzoate,



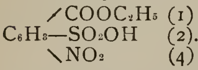
$$C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2OAg\\ \diagdown NO_2\end{array}(?).—$$

When an aqueous solution of the acid methyl ether is treated with freshly precipitated silver carbonate, and the solution, filtered from excess of silver carbonate, evaporated to dryness on the water-bath, the silver salt of the acid methyl ether is obtained. On account of its great solubility and the ease with which it is blackened on exposure to light, no analysis was attempted, but from its reaction with ethyl iodide, there can be little doubt that the anhydrous salt has the composition



$$C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2OAg.\\ \diagdown NO_2\end{array}$$

Acid Ethyl Ether of (p)-nitro-sulpho-benzoic Acid,



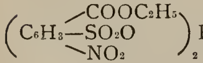
$$C_6H_3\begin{array}{ll}\diagup COOC_2H_5 & (1)\\ -SO_2OH & (2)\\ \diagdown NO_2 & (4)\end{array}$$

.—This acid is most easily made by boiling about 10 parts by weight of the chloride of (*p*)-nitro-sulpho-benzoic acid with 25 parts by weight of absolute alcohol. The excess of alcohol is evaporated off, and there remains a thick syrup which, on standing, becomes crystalline.

Like the corresponding methyl compound, this acid crystallises from dilute alcohol in fine white needles which blacken at a high temperature. The acid ethyl ether is a strong acid, and forms salts which crystallise well.

The following have been made and analysed:

Barium Ethyl-(p)-nitro-sulpho-benzoate,



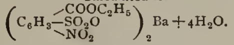
$$\left(C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2O\\ \diagdown NO_2\end{array}\right)_2Ba + 4H_2O.$$

—The free acid was neutralised with barium carbonate, the hot solution was filtered from the excess of carbonate and allowed to cool, when the barium salt crystallised out in long white needles which show a strong tendency to concentric grouping.

It is easily soluble in hot water, and is but slightly soluble in the cold. The following is the result of analysis:

0.2366 gram of the salt lost on heating to 175° C. 0.0225 gram.
0.2141 gram of the dried salt gave 0.0734 gram $BaSO_4$.

Calculated for

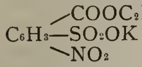


$\left(C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2O\\ \diagdown NO_2\end{matrix}\right)_2 Ba + 4H_2O.$

	Calculated for $\left(C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2O\\ \diagdown NO_2\end{matrix}\right)_2 Ba + 4H_2O.$	Found.
H_2O	9.51 per cent.	9.50 per cent.

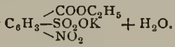
	Calculated for the dried salt.	Found.
Ba	20 per cent.	20.14 per cent.

Potassium Ethyl-(p)-nitro-sulpho-benzoate,



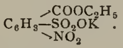
$C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2OK\\ \diagdown NO_2\end{matrix} + H_2O$.—This salt can easily be obtained by neutralising the free acid with potassium carbonate. It is easily soluble in hot water, less so in cold. An analysis gave the following numbers:

0.2569 gram of the salt lost on heating to 140° C. 0.0138 gram.
0.2431 gram of the dried salt gave 0.0681 gram K_2SO_4.



$C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2OK\\ \diagdown NO_2\end{matrix} + H_2O.$

	Calculated for $C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2OK\\ \diagdown NO_2\end{matrix} + H_2O.$	Found.
H_2O	5.42 per cent.	5.33 per cent.



$C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2OK\\ \diagdown NO_2\end{matrix}.$

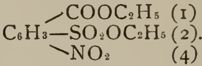
	Calculated for $C_6H_3\begin{matrix}\diagup COOC_2H_5\\ —SO_2OK\\ \diagdown NO_2\end{matrix}.$	Found.
K	12.59 per cent.	12.62 per cent.

Copper Ethyl-(p)-nitro-sulpho-benzoate.—The copper salt of the acid ethyl ether can be best made by treating the barium salt with an equivalent quantity of copper sulphate. It is very soluble, and crystallises after long standing in light green leaflets, and, like the copper salt of the acid methyl ether, it forms a beautiful cuprammonium compound when treated with strong ammonia.

Silver Ethyl-(p)-nitro-sulpho-benzoate.—This salt has been prepared in considerable quantity by neutralising the aqueous solution of the acid ethyl ether with freshly precipitated silver carbonate. The excess of silver carbonate is filtered off and the filtrate evaporated to dryness on the water-bath. The silver salt thus obtained is very soluble; on long standing in the dark it crystallises from water in fine silken needles. It blackens on exposure to light, and on this account was not analysed.

The acid ethers of (*p*)-nitro-sulpho-benzoic acid can also be prepared by treating the free acid with a primary alcohol and hydrochloric acid gas.

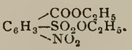
ETHERS AND MIXED ETHERS OF (*p*)-NITRO-SULPHO-BENZOIC ACID.

Di-ethyl (*p*)-*nitro-sulpho-benzoate*,  $C_6H_3\begin{array}{l}\diagup COOC_2H_5\ (1)\\ -SO_2OC_2H_5\ (2)\\ \diagdown NO_2\ \ (4)\end{array}$.—The dry silver salt of the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid was heated to 100° C. with ethyl iodide for two hours. The pressure bottle in which the reaction had been carried on was then allowed to cool and the contents extracted with 95 per cent. alcohol.[1] The extract was filtered hot and allowed to stand, when a substance crystallised out in thin white leaflets. The substance thus obtained is but slightly soluble in cold alcohol, easily soluble in hot alcohol. The substance shows a strong crystallising power. When pure it crystallises from alcohol in leaflets of a very beautiful pearly lustre. It is precipitated from its alcoholic solution by water, in which it is insoluble. When heated with water it melts to a clear, heavy oil which solidifies again when the water becomes cold. It also dissolves quite readily in ether, from which it separates on slow evaporation in bright, transparent crystals.

The thin leaflets obtained from alcohol were found to melt at 65°–66° C. uncorrected.

A determination of the sulphur in the compound was made by Liebig's method, with the following result:

0.1893 gram of the ether gave 0.1464 gram $BaSO_4$.

	Calculated for  $C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OC_2H_5.\\ \diagdown NO_2\end{array}$	Found.
S	10.56 per cent.	10.61 per cent.

Action of Ammonia on the Di-ethyl Ether.

About 5 grams of the ether were dissolved in a concentrated alcoholic solution of ammonia, and the solution heated to 100° C. in a pressure bottle for about an hour. A compound readily soluble in water was obtained in this way, which, on standing over sulphuric acid, crystallised from its aqueous solution in large, transparent, tabular plates. The substance was found to dissolve in a solution of caustic potash with liberation of ammonia, even in the cold, and on heating this alkaline solution and evaporating, the neutral potassium salt of (*p*)-nitro-sulpho-benzoic acid crystallised out.

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[1] It has since been found better to use absolute ether for the extraction.

These crystals were dissolved in a small quantity of water, and a drop or two of strong hydrochloric acid added, when the characteristic acid potassium salt of (*p*)-nitro-sulpho-benzoic acid crystallised out in fine white needles.

From this it seems that the action of ammonia on the ether is simply that of saponification.

Action of Water on the Di-ethyl Ether.

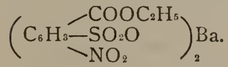
About 2 grams of the ether were boiled with distilled water for about an hour; at the end of that time the resulting acid liquid was neutralised with barium carbonate. The solution was filtered from the excess of barium carbonate and evaporated. On cooling, the barium salt of the acid ethyl ether crystallised out. This salt gave the following numbers on analysis, and was found to be identical in every respect with the salt described on p. 190:

	Found.
Ba	20.09 per cent.
H_2O	9.60 "

Action of Alcohol on the Di-ethyl Ether.

1 gram of the di-ethyl ether was dissolved in absolute alcohol, and the solution heated to 100° C. in a pressure bottle for about an hour. At the end of that time the alcohol was evaporated off, and the acid syrup thus obtained dissolved in water and neutralised with barium carbonate.

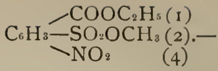
The barium salt thus obtained was found, like the one just described, to be the barium salt of the acid ethyl ether,



$$\left(C_6H_3\begin{matrix}\diagup COOC_2H_5\\ -SO_2O\\ \diagdown NO_2\end{matrix}\right)_2Ba.$$

This easy saponification of one of the ether residues by one equivalent of alkali, by water and by alcohol, is very interesting, and is characteristic of all the ethers of (*p*)-nitro-sulpho-benzoic acid, and is, as I shall soon show, a reaction which affords the best experimental evidence of the correctness of the views expressed concerning their constitution.

Ethyl-methyl (*p*)-*nitro-sulpho-benzoate*,



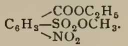
$C_6H_3\left\langle\begin{array}{ll}COOC_2H_5 & (1)\\ SO_2OCH_3 & (2)\\ NO_2 & (4)\end{array}\right.$.—

The silver salt of acid ethyl-(*p*)-nitro-sulpho-benzoate was treated with the calculated amount of methyl iodide. When these substances were brought together in this proportion, reaction took place at once, with the formation of silver iodide and the ethyl-methyl ether. In order to insure its completion, however, the pressure bottle in which these two substances had been brought together was heated on the water-bath for half an hour.

The contents of the pressure bottle were then extracted with anhydrous ether, the extract filtered and allowed to evaporate slowly, when the ethyl-methyl ether crystallised out. This compound, like the di-ethyl ether, is insoluble in water. It is easily soluble in alcohol, from which it crystallises in short, thick, rounded white crystals. It is easily soluble in ether, from which it crystallises in flat, slightly elongated, transparent prisms. After several recrystallisations from alcohol the ether melted at 80° C. (uncorrected) to a clear liquid, which solidified again at 65° C.

The sulphur was determined by Liebig's method, with the following result:

0.2051 gram substance gave 0.1682 gram $BaSO_4$.



	Calculated for $C_6H_3\left\langle\begin{array}{l}COOC_2H_5\\ SO_2OCH_3.\\ NO_2\end{array}\right.$	Found.
S	11.07 per cent.	11.26 per cent.

Experiments on the saponification of the ethyl-methyl ether were made with the view of determining which alkyl group remained in the compound and which was split off.

Action of Caustic Potash on the Ethyl-methyl Ether.

About 1 gram of the ether was treated with dilute caustic potash, in the proportion of 1 molecule to 1 molecule of the ether. The saponification took place easily, and a quantitative yield of a potassium salt was obtained which gave the following numbers on analysis:

0.2120 gram salt lost on heating to 140° C. 0.0116 gram.

0.2004 gram dried salt gave 0.0561 gram K_2SO_4.

	Found.
H_2O	5.47 per cent.
K	12.87

These figures agree sufficiently well with those calculated for the potassium salt of the acid ethyl ether. (See p. 191.)

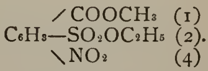
Action of Water on the Ethyl-methyl Ether.

When the ethyl-methyl ether is heated with distilled water it first melts to a clear heavy oil which, after long boiling and considerable agitation, goes into solution. The solution, which now reacts acid, is neutralised with barium carbonate, filtered and evaporated, when the characteristic barium salt of the acid ethyl ether crystallises out.

Action of Alcohol on the Ethyl-methyl Ether.

Hot absolute alcohol readily dissolves the ethyl-methyl ether, and when this solution was heated in a pressure bottle for about an hour at the temperature of the water-bath, the acid ethyl ether of (*p*)-nitro-sulpho-benzoic acid was formed. This was proved by neutralising the acid liquid with barium carbonate, and analysing the barium salt thus formed.

From these experiments it is clear that the ethyl group is the one which is held most firmly in the compound, inasmuch as the acid ethyl ether is obtained when the mixed ether is treated with one equivalent of caustic potash, or with even such mild saponifying agents as water and alcohol.

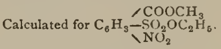
Methyl-ethyl (p)-nitro-sulpho-benzoate, 

$$C_6H_3\begin{cases}COOCH_3 & (1)\\ SO_2OC_2H_5 & (2).\\ NO_2 & (4)\end{cases}$$

—The silver salt of acid methyl-(*p*)-nitro-sulpho-benzoate was treated with ethyl iodide in a pressure bottle at the temperature of the water-bath, in the proportion of 1 mol. of the silver salt to 1 mol. of the iodide. The reaction took place readily, with abundant formation of silver iodide. After an hour's heating, the contents of the bottle were extracted with anhydrous ether, the extract filtered and allowed to evaporate, when the methyl-ethyl ether was obtained.

Like its isomer, and like the di-ethyl ether, it is insoluble in cold water, it melts to a clear oil when the water is heated, and is slowly decomposed into alcohol and the acid methyl ether, both of which pass into solution. It is easily soluble in hot alcohol, less so in cold, so that on cooling it separates from the hot concentrated alcoholic solution in clusters of fine white needles. In this respect it differs from its isomer, which always crystallises from alcohol in short compact crystals, and never in needles. It is also easily soluble in ether, from which it crystallises in fine white needles which, when pure, were found to melt at 68° C. uncorrected. A sulphur determination by Liebig's method gave the following result:

0.2189 gram of substance gave 0.1772 gram $BaSO_4$.



	Calculated for $C_6H_3\begin{array}{l}\diagup COOCH_3\\ -SO_2OC_2H_5.\\ \diagdown NO_2\end{array}$	Found.
S	11.07 per cent.	11.10 per cent.

Action of Water on the Methyl-ethyl Ether.

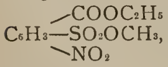
When the methyl-ethyl ether is heated with distilled water, it first melts to a clear heavy oil which, on continued shaking, passes into solution. This solution was found to react acid, and was accordingly neutralised with barium carbonate, when a barium salt identical with the one described on page 187 was obtained.

	Found.
H_2O	7.9 per cent.
Ba	20.7

These figures agree sufficiently well with those required by the salt above referred to.

Action of Absolute Alcohol on the Methyl-ethyl Ether.

About 5 grams of the ether were dissolved in absolute alcohol, and the solution heated in a pressure bottle at 100° C. for an hour. At the end of that time the solution was found to react acid, and was neutralised with barium carbonate. The barium salt of the acid methyl ether was obtained. This easy saponification of one of the ether residues in these mixed ethers by one equivalent of caustic potash, by water and even by alcohol, with the production of the acid ethyl ether from the one, and the acid methyl ether from the other, exhibits in a striking way the character of the isomerism which is here presented, and shows clearly that in the compound first described, viz. the ethyl-methyl ether,



$C_6H_3\begin{array}{l}\diagup COOC_2H_5\\ -SO_2OCH_3,\\ \diagdown NO_2\end{array}$ the methyl group is less firmly held in the molecule than the ethyl, whereas in the other the reverse of this is true.

GENERAL CONSIDERATIONS.

The careful study of the saponification phenomena exhibited by these mixed ethers not only shows in a clear way the character of their isomerism, but it has also enabled me to explain the constitution of these and other compounds described in the preceding pages, and to interpret certain reactions which otherwise would scarcely admit of a rational explanation.

It has been shown that when these mixed ethers are treated either with one equivalent of caustic potash, with water or with alcohol, one alkyl group is easily split off, whereas the other remains in the compound, and that an *acid* ether in the place of a *neutral* ether results.

Further, it has been shown that the alkyl group which enters the compound last is the first to leave it when the ether is saponified. This would seem to indicate that in both cases it is in combination with the same acid residue. If this be true, then with what acid residue is it in combination: is it united to the carbonic acid portion or to the sulphonic acid portion of this dibasic acid?

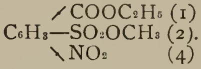
The answer to this question is to be found in the comparative study of the conduct of the ethers of the carbonic and sulphonic acids respectively. It is well known that the ethers of the carbonic acids are stable substances; it is true they can all be saponified by means of the strong alkalies, but with water no reaction takes place, or if it does, it is only to an inappreciable extent.

In the case of the lactones, which may be regarded as ethers of carbonic acids in which the ether formation has taken place in one and the same molecule, water does act as a saponifying agent; but even here this reaction has been shown by Fittig to be a reversible one, and consequently takes place only to a limited extent.

This exception, however, if it is to be regarded as such, is not to the point, inasmuch as the substances here treated of cannot possibly be considered lactones. Towards alcohol the ethers of the carbonic acids are perfectly stable, no reaction whatever taking place when these substances are brought together.

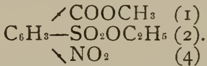
With the ethers of the sulphonic acids, however, the case is entirely different. These substances are not only acted on by strong alkalies with the greatest ease, but they are also easily decomposed by water into the free acid and alcohol. Regarding their conduct towards alcohol I have been unable to find any statements, but when we consider the ease with which alcohol acts on the acid ethers of sulphuric acid it seems highly probable that these substances would undergo similar transformations.

In the light of all this it seems highly probable that in the ethyl-methyl ether described on p. 194 we have the methyl replacing the acid hydrogen of the sulphonic acid portion of the compound, inasmuch as the *acid ethyl ether* is obtained when this compound is treated with water or with alcohol. These facts find their simplest explanation in this formula,

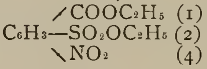


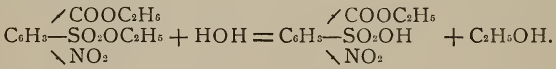
$$C_6H_3\begin{array}{ll} \diagup COOC_2H_5 & (1) \\ -SO_2OCH_3 & (2). \\ \diagdown NO_2 & (4) \end{array}$$

In the methyl-ethyl ether, on the other hand, we have found that the reverse of this is true; on treating this compound with water, the acid methyl ether was obtained. This decomposition can be most easily explained by means of this formula,

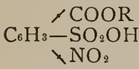


$$C_6H_3\begin{array}{ll} \diagup COOCH_3 & (1) \\ -SO_2OC_2H_5 & (2). \\ \diagdown NO_2 & (4) \end{array}$$

The formula  $C_6H_3\begin{array}{ll} \diagup COOC_2H_5 & (1) \\ -SO_2OC_2H_5 & (2) \\ \diagdown NO_2 & (4) \end{array}$ for the di-ethyl ether is also in strict accordance with the facts, inasmuch as it also is partially saponified when treated with water, the acid ethyl ether being the result of the action,

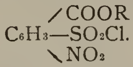


$$C_6H_3\begin{array}{l} \diagup COOC_2H_5 \\ -SO_2OC_2H_5 \\ \diagdown NO_2 \end{array} + HOH = C_6H_3\begin{array}{l} \diagup COOC_2H_5 \\ -SO_2OH \\ \diagdown NO_2 \end{array} + C_2H_5OH.$$

From this it is clear that the acid ethers of (*p*)-nitro-sulpho-benzoic acid are to be regarded as made up in this way,  $C_6H_3\begin{array}{l} \diagup COOR \\ -SO_2OH \\ \diagdown NO_2 \end{array}$, in which R represents any alkyl.

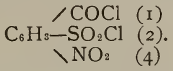
This formula for these compounds also finds support in the fact that the acid ethyl ether can be prepared by treating (*p*)-nitro-sulpho-benzoic acid with alcohol and gaseous hydrochloric acid.

The structure of the compounds described on pages 182, 184 also admits of an easy explanation. We have seen from their reactions that, notwithstanding the fact that they possess to some extent the properties of ethereal salts, they are nevertheless to be regarded as true acid chlorides. The ease with which they pass into the corresponding acid ethers of (*p*)-nitro-sulpho-benzoic acid shows that they must have the constitution represented by this formula,



$$C_6H_3\begin{array}{l}\diagup COOR\\ —SO_2Cl.\\ \diagdown NO_2\end{array}$$

The ease with which nitro-benzoic sulphinide is formed from these compounds by treatment with ammonia can easily be explained by the aid of this formula. It is also clear from the reactions which have already been described that the structure of the chloride of (*p*)-nitro-sulpho-benzoic acid can be best represented by this formula,



$$C_6H_3\begin{array}{ll}\diagup COCl & (1)\\ —SO_2Cl & (2).\\ \diagdown NO_2 & (4)\end{array}$$

That the chlorine atoms in this compound are not held in the same way is evident, inasmuch as but one of them is replaced, and not both, when the chloride is treated with absolute alcohol.

The easy formation of nitro-benzoic sulphinide from the compounds thus prepared, and from the chloride of (*p*)-nitro-sulpho-benzoic acid itself, also finds a simple explanation on the assumption that the formula above given correctly represents the structure of this chloride.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, *March*, 1888.

REVIEWS AND REPORTS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

2. ALKALI MANUFACTURE.

The most striking change in the alkali industry which the last ten years have witnessed is the rapid growth and extension of the ammonia-soda process. Works have been established by the Solvays in Germany, Austria, Russia, and the United States, and the production of ammonia-soda has rapidly increased, while the

Leblanc-soda industry has steadily declined. Between the years 1880 and 1886 the amount of ammonia-soda produced in the United Kingdom increased from 18,800 tons to 85,000 tons, while the production of Leblanc-soda decreased during the same period from 266,000 tons to 165,782 tons.

A paper by the late Mr. Walter Weldon, read before the Society of Chemical Industry on the eighth of January, 1883,[1] gave a very interesting and complete review of the position in which these two rival processes stood at that time, and stated the probable tendency of the whole alkali industry in the near future. It will be of interest to inquire briefly to what extent these forecasts have been realised.

Mr. Weldon described the failing condition of the Leblanc-soda industry and the threatening attitude of the ammonia process, and stated that soda was then being made by the latter process at a cost fully one pound sterling lower than by the former. Nevertheless he was of the opinion that the Leblanc process would soon be greatly cheapened, and would thus be enabled to hold its own. The economies which he believed would produce this result are, 1st, cheaper pyrites; 2d, cheaper fuel in the form of gas made from waste coal, with recovery of tar and ammonia; and 3d, recovery of sulphur from the alkali-waste.

Within a few months after the presentation of this paper, the Tharsis Company broke away from the combination of Spanish pyrites producers by which the price had been maintained at 6d. per unit of sulphur, and reduced the price to 3d. per unit. It is probable that a still further reduction may be made, and that the Spanish producers are in a position to furnish English sulphuric acid makers with pyrites free of charge, merely stipulating that the cinders shall be returned to be treated for copper. It would, of course, be cheaper to burn the pyrites in Spain, letting the sulphur go to waste, but the great damage to agriculture which this operation has caused in the past has led to the enactment of stringent regulations which will make it impossible to carry on this process on a large scale.

Recovery of Sulphur from Alkali-waste.—The final success of a practical method of recovering the sulphur from tank-waste has been announced during the past year. As this discovery is likely to exert an important influence on the alkali and sulphur industries of the world, it may be of interest to review briefly the history of sulphur recovery.

All the sulphur used in making acid for the alkali industry finally appears at the end of the process, chiefly as calcium sulphide, in the tank-waste. In England there are produced yearly one and one-half million tons of this waste, containing 10 to 14 per cent. of sulphur. This material is not only useless, but it is a source of intolerable nuisance on account of the odors which rise from it and the pollution of the streams which it causes when allowed to accumulate near water-courses. The effective disposal of this immense mass of waste is a great source of expense. Many attempts have been made to extract the sulphur from the material and at the same time render the waste inoffensive. The methods of Schaffner and Mond depend upon the more or less complete oxidation of the waste, and the separation of sulphur from the resulting mixture of calcium sulphide and thiosulphate by treatment with hydrochloric acid. These processes have been used to some extent, especially in Germany, for many years, but resulted in the recovery of not more than half the sulphur of the waste. They cannot be said to have been commercially successful.

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[1] Journal of the Soc. of Chem. Ind. 1883; reprinted in the Amer. Chem. J. Jan. 1883, and Chem. News, Feb. 9, 1883.

Schaffner and Helbig's process, introduced in 1878, was designed to recover all the sulphur in the form of hydrogen sulphide. This is accomplished by heating the waste in tanks with a solution of magnesium chloride, in which operation the following reaction takes place:

$$CaS + MgCl_2 + 2H_2O = CaCl_2 + Mg(OH)_2 + H_2S.$$

By passing carbon dioxide into the resulting solution of calcium chloride containing magnesium hydroxide in suspension, magnesium chloride is regenerated, to be used over again, and calcium carbonate is precipitated in a form well adapted for use in the black ash process:

$$CaCl_2 + Mg(OH)_2 + CO_2 = CaCO_3 + MgCl_2 + H_2O.$$

The hydrogen sulphide given off in the first reaction is in part burned to sulphur dioxide, and this gas brought into contact with the remaining hydrogen sulphide in a solution of calcium chloride; the well known reaction,

$$2H_2S + SO_2 = 3S + 2H_2O$$

takes place. The effect of the calcium chloride is to cause the sulphur to separate in a flocculent form, in which it settles readily, and to prevent the formation of polythionic acids, which would cause loss.

This process was to some extent introduced into England; the production of sulphur by the action of sulphur dioxide and hydrogen sulphide was, however, never satisfactorily carried out in practice, and the recent great reduction in the price of pyrites caused attempts to use the process to be generally abandoned.

Weldon proposed to reduce the amount of magnesium chloride necessary in the first reaction to one-half by employing Krausshaar's process of heating the tank-waste with water under pressure, by which the sulphide is converted into hydrosulphide and hydrate:

$$2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

The calcium hydrate was to be filtered out, and the solution of the hydrosulphide treated with magnesium chloride, of which only one equivalent would be required to two of hydrogen sulphide obtained; the magnesium hydrate, being free from the impurities of the tank-waste, would be a salable product.

The decomposition of calcium sulphide by carbon dioxide has long been known, and was the subject of many experiments by Gossage and others more than fifty years ago. The great objection to the use of this method has always been the irregular composition and amount of the hydrogen sulphide liberated. In 1882 Opl proposed to pass carbon dioxide into the tank-waste suspended in water, and to conduct the hydrogen sulphide given off into fresh waste, forming calcium hydrosulphide, which could then be treated with magnesium chloride as in Schaffner and Helbig's process. In other words, Opl proposed to accomplish by carbon dioxide the same result as Krausshaar by heating with water, namely, the concentration of the sulphur of the waste and separation of half the lime.

The process introduced by Chance Bros.[1] is in some respects an extension of that of Opl, and happily overcomes the practical difficulties which opposed the early experiments of Gossage and others who sought to accomplish the decomposition of tank-waste by carbon dioxide. This process seems to furnish a complete solution of the long standing problem of sulphur recovery.

Tank-waste suspended in water is introduced into vertical cylinders, through a series of which the gases from closed lime-kilns, consisting of about 70 per cent. nitrogen and 30 per cent. carbon dioxide, are pumped under pressure. The hydrogen sulphide given off in the first tanks is absorbed by the waste in the succeeding ones, with the formation of hydrosulphide, while the inert nitrogen passes through the series and is allowed to escape. When the gas coming from one of the tanks contains a sufficient proportion of hydrosulphide (shown by burning well in a Bunsen lamp), connection is made with a large gasholder, and the gas collected and stored for use. This gas is of constant composition, contains over 30 per cent. of hydrogen sulphide, and is of suitable strength for burning to sulphur dioxide for the manufacture of sulphuric acid, or for the preparation of sulphur by the "Claus kiln," in which the hydrogen sulphide is burned with the necessary amount of air to produce water and free sulphur, according to the reaction,

$$H_2S + O = H_2O + S.$$

Mr. Chance, in the paper mentioned above, describes the working of this kiln as follows: "The process is performed by mixing sulphuretted hydrogen with a *regulated quantity* of air, and sending the mixture through a layer of anhydrous oxide of iron, which, by the heat generated by the reaction itself, is maintained at a dull red heat, the oxide of iron itself undergoing no change. Free sulphur, accompanied by the vapor of water, passes off, the sulphur being obtained in the fused or sublimed form, according to the temperature of the kiln and of the depositing chambers."

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[1] J. Soc. Chem. Ind. 1888, p. 163.

Prior to March, 1888, the firm named had recovered by the above process 90 per cent. of the sulphur from over 3000 tons of waste, and claim that the operation of obtaining hydrogen sulphide and burning it to sulphur or sulphuric acid is in every respect cheap, simple and satisfactory. No fuel is required in any part of the process. The precipitated calcium carbonate is as suitable for the black ash process as that obtained by Schaffner and Helbig's method, and its value for this purpose is increased by the fact that it contains about two per cent. of sodium salts. The sulphuric acid obtained is extremely pure and free from arsenic. It is estimated that if this process were universally adopted, at least 100,000 tons of sulphur could be annually recovered, which is nearly equal to the whole amount imported from Sicily into England and America.

It would seem that this process, with the present low price of pyrites and the prospect of still further reduction, might turn the tide in favor of the Leblanc process. That the fall in the price of pyrites which has already taken place is not in itself sufficient, is shown by the continued steady decrease in the production of Leblanc soda in England since 1883. It remains to be seen to what extent the Chance process of sulphur recovery may change for the better the position of Leblanc soda-makers.

The Parnell and Simpson Alkali and Sulphur Process.—A very interesting novelty in the alkali industry is the combined Leblanc and Ammonia process of Parnell and Simpson, which has been worked experimentally in England since 1885, and the details of which have just been published.[1] In this process sodium bicarbonate is obtained by treating brine and *ammonium sulphide* with lime-kiln gases, and the resulting ammonium chloride is reconverted into sulphide by heating with Leblanc tank-waste. The waste and ammonium chloride are heated in vats by steam:

$$CaS + 2NH_4Cl = CaCl_2 + (NH_4)_2S.$$

The ammonium sulphide distills off and is absorbed in strong brine. The carbonating operation takes place in two stages, in the first of which no hydrogen sulphide is given off and the inert gases are allowed to escape:

$$(NH_4)_2S + H_2O + CO_2 = HNH_4CO_3 + HNH_4S.$$

In the second stage, complete conversion into bicarbonate takes place, with liberation of strong hydrogen sulphide:

$$HNH_4S + CO_2 + H_2O = HNH_4CO_3 + H_2S.$$

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[1] J. Soc. Chem. Ind. 1889, p. 11.

The bicarbonate reacts with the salt present, producing sodium bicarbonate; the hydrogen sulphide is partly burned to sulphur dioxide, which is made to act on the remainder of the hydrogen sulphide, producing sulphur, as in the Schaffner and Helbig process. The inventors claim to have made improvements by which the latter reaction can be successfully carried out.

This process virtually makes a modified ammonia-soda process a means of recovering the sulphur from Leblanc waste. The advantage of this combination over a Leblanc plant recovering sulphur by the Chance process, and an ordinary ammonia-soda works, would be merely in the saving of the lime needed to regenerate the ammonia in the latter process. As a new method for the recovery of sulphur from tank-waste, the Parnell and Simpson process may, however, have an important future.

The Weldon-Pechiney Process.—Meanwhile there are two important directions from which further help may come to the ammonia-soda industry, the first of which is the Weldon-Pechiney chlorine process, now being successfully worked at Salindres, in the south of France.[1] This is based upon a reaction which has long been known, the decomposition of moist magnesium oxychloride by heat, giving free chlorine and hydrochloric acid.

Magnesium chloride is obtained by dissolving magnesia in the hydrochloric acid produced in the process. The solution of the chloride is evaporated to a certain point, and an equivalent quantity of magnesia added. The mass becomes solid, is broken up into lumps and partially dried. At this stage the oxychloride contains about 25 per cent. of water. It is charged into narrow retorts intensely heated by gas. About 80 per cent. of the chlorine contained is given off, of which about one-half is free chlorine. The hydrochloric acid is condensed by water, and the chlorine used for making chlorate.

By this method hydrochloric acid may be made to yield over 80 per cent. of its chlorine in the free state, while by the Weldon process (recovering the manganese dioxide), only 33 per cent., and by the Deacon process only 40 to 50 per cent. are obtained.

The effect of this process upon the Leblanc-soda industry depends upon the fact that it may furnish a cheap source of chlorine for making bleaching powder, thus diminishing the value of the chief bye-product of the Leblanc process. The Weldon-Pechiney process is especially applicable in places where magnesium chloride is a waste product. It is estimated that if established at Stassfurt, where great quantities of waste magnesium chloride are produced, bleaching powder could be manufactured there at a cost of five pounds sterling per ton, while the present cost of production in England is thirteen pounds per ton.

Recovery of Chlorine in the Ammonia-Soda Process.—It is generally acknowledged that if the chlorine of the salt treated by the ammonia-soda process, which is now wholly lost as calcium chloride (of which more than a ton is discarded for every ton of soda-ash produced), could be cheaply recovered and made available for making bleaching powder, etc., the final supremacy of the ammonia-soda process would be assured. Many attempts to accomplish this have been made, but as yet no commercially successful process has been made public. Solvay has been engaged for years in experiments on the decomposition of calcium chloride by means of silica and clay at high temperature, while Mond asserts his full confidence in the final success of his plan of decomposing ammonium chloride into ammonia and hydrochloric acid. This is to be effected by passing ammonium chloride vapor over heated nickel oxide (or other oxides), by which hydrochloric acid is absorbed and ammonia liberated; the nickel chloride is then decomposed by highly heated steam or air, with the reformation of the oxide. Another plan is that of Twynam, who converts calcium chloride into the oxychloride by addition of lime, and then decomposes the oxychloride by heating in a current of air, exactly as the magnesium oxychloride is decomposed in the Weldon-Pechiney chlorine process. Mond has just patented a method of obtaining ammonia and chlorine from ammonium chloride,[1] which is practically an application of the Weldon-Pechiney to the ammonia-soda process. Ammonium chloride vapor is passed over heated magnesia to which 5 or 10 per cent. of sodium or potassium chloride has been added. Ammonia and steam are produced, and magnesium chloride remains. The latter is then decomposed by heating intensely in a current of air; chlorine is given off, and magnesium oxide is left behind to be again treated with ammonium chloride. No account of the practical working of these processes on a large scale has, however, been made known.

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[1] Dewar, J. Soc. Chem. Ind. Dec. 1887.

The Ammonia-Alkali Industry.—In conclusion, it may be of interest to consider briefly the present state of the alkali industry in the United States.

A small amount of Leblanc soda was formerly made in this country, but so far as is known to the writer, this industry does not exist here at present. Caustic soda has been made by the Cryolite process for many years by the Pennsylvania Salt Manufacturing Co. at their works at Natrona, near Pittsburg. This company enjoyed for a long period the right to two-thirds of the Cryolite mined at Evigtok, Greenland.

Nearly all the soda-ash used for glass and soap making in this country was until very lately imported, chiefly from England. In 1882 the Solvay Process Co. was established at Syracuse, N. Y., and soon after that time the manufacture of ammonia-soda was commenced at these works. The production rapidly increased, and in 1888 amounted to over 60,000 tons, or one-third of the total quantity of soda consumed in the United States. Caustic soda is also made by this firm on an extensive scale. Explorations undertaken by the Syracuse Company have resulted in the discovery of valuable deposits of salt, sufficient to supply the needs of the works indefinitely.

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[1] J. Soc. Chem. Ind. 1888, p. 845.

Dr. Francis Wyatt, in the articles on Chemistry Industry mentioned above, urges the adoption of the Leblanc process in this country, as best suited to the peculiar conditions which here prevail. At the time of the publication of his papers, the success of the Chance process of sulphur recovery, which is undoubtedly of great importance in this connection, had not yet been announced. It would seem that the establishment of a Leblanc plant in a suitable locality in this country, using Spanish pyrites, working the cinders for copper and silver, manufacturing bleaching powder and recovering the sulphur by Chance's process, must be successful. Over 50,000 tons of bleaching powder and 85,000 tons of Sicilian sulphur are annually imported into the United States; these products would therefore find a ready market.

The rapid development of the ammonia-soda industry at Syracuse, however, shows that that process is well adapted to the needs of the country, and it is probable that these works, or branch establishments located at other places, will, in the near future, supply the whole American demand for alkali.

SPENCER B. NEWBURY.

REPORT ON SOME RECENT ADVANCES IN PHYSIOLOGICAL CHEMISTRY.

In a volume of "Studies" recently issued from the laboratory of physiological chemistry of Yale University,[1] there are given the results of nine investigations relating to subjects of more or less importance in physiological chemistry. Of these, three deal with the primary cleavage products formed from elastin, casein and myosin by the action of the proteolytic ferments pepsin and trypsin, and also by the hydrolytic action of boiling dilute acid.

On heating moist elastin with water containing a trace of hydrochloric acid for some hours at or near 100° C., it was found that the elastin soon commences to swell, and after a time is converted into a semi-gelatinous mass, a portion of which, as the heating is continued, becomes soluble and passes into the acid fluid. The liquid gives no reaction with tannic acid for gelatin, but does give a strong biuret reaction, and with an excess of caustic alkali shows a heavy turbidity. The soluble matter consists of two distinct bodies called respectively proto- and deutero-elastose, which bear the same relation to elastin that the corresponding albumoses[2] do to albumin. Further, like the albumoses, they are completely precipitated from a neutral fluid by saturation with ammonium sulphate. Proto-elastose is precipitated by saturation of a neutral fluid with sodium chloride, while deutero-elastose is precipitated from a salt-saturated solution by addition of dilute acetic acid. Proto-elastose is readily soluble in cold water, but only slightly in hot water. In a neutral solution, heat produces a turbidity or coagulum which disappears as the fluid cools. Long-continued evaporation of an aqueous solution of proto-elastose leads to a separation of more or less of the substance as a gummy mass. Concentrated mineral acids produce precipitates soluble in excess of acid. Alcohol partially precipitates the substance, and phosphotungstic and picric acid both produce precipitates. The elastose is but slightly, if at all, diffusible, and in composition does not differ essentially from the original elastin. Deutero-elastose, on the other hand, contains a smaller percentage of carbon than elastin, and further differs from proto-elastose in that it is completely soluble in hot and cold water, and is not precipitated by the mineral acids, by alcohol, nor by acetic acid and potassium ferrocyanide. It is also more readily diffusible.

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[1] Studies from the laboratory of physiological chemistry, Sheffield Scientific School of Yale University, Vol. III, edited by R. H. Chittenden, Ph. D., professor of physiological chemistry. New Haven, January, 1889.

[2] See this Journal **6**, 31 and 101.

By the action of pepsin-hydrochloric acid at the body temperature, powdered elastin was found quite easily digestible,[1] and although apparently no true peptones were formed (*i. e.* soluble products not precipitated by saturation with ammonium sulphate), large amounts of proto- and deutero-elastose were obtained similar in reactions to those already described. Bodies of like nature, but of somewhat different composition, were also formed by digestion of pure elastin with an alkaline solution of trypsin.

The composition of the several elastoses and their relation to elastin is shown in the following table :

	Elastin *A.*	Elastin *B.*	Action of acid water at 100° C.		Action of pepsin-hydrochloric acid.		Action of alkaline trypsin solution.	
			Protoelastose.	Deutero-elastose.	Protoelastose.	Deutero-elastose.	Protoelastose.	Deutero-elastose.
C	54.24	54.08	54.27	53.26	54.52	53.11	53.05	54.65
H	7.27	7.20	7.12	7.12	7.01	7.08	7.02	7.04
N	16.70	16.85	17.02	16.70	16.96	16.85	16.88	16.55
S	..	0.30	..	..	..	..	..	..
O	21.79	21.57	21.59	22.92	21.51	22.96	23.05	21.76
Ash	0.90	0.31	1.47	2.01	1.34	5.02	7.38	5.45

Casein, on being subjected to the action of artificial gastric juice, is decomposed into soluble caseoses and peptone, but in every digestion there invariably remains a certain amount of an insoluble, pasty, grayish-white substance, which is not susceptible to the action of pepsin-acid, no matter how long continued. This insoluble substance, noticeable to a greater or less extent in the pepsin digestion of all proteids, but particularly so with casein, was named casein-dyspeptone by Meissner, and later, in 1870, was fully described by Lubavin,[1] who looked upon it as a mixture of two bodies, one of which was considered as containing 4.6 per cent. of phosphorus and having the formula $C_{27}H_{47}N_6PO_{11}$. A careful study of this dyspeptone, prepared from pure casein by a large number of separate digestions with pepsin-hydrochloric acid, has resulted in showing that this substance is a mixture of calcium phosphate with a hydration-product of casein, the hydrochloric acid compound of which is insoluble in water and dilute acid. The so-called dyspeptone, when freed from acid, is quite readily soluble in water, the solution remaining unchanged on boiling. It is precipitated by saturation of its aqueous solution with ammonium sulphate, but not by sodium chloride. Addition of acetic acid to the salt-saturated fluid gives the usual precipitate of dyspeptone. Acetic acid, when added to an aqueous solution of the substance, gives a heavy white precipitate, insoluble in moderate excess of acid, but entirely soluble in a large excess on application of heat. Addition of potassium ferrocyanide to the clear acid fluid gives only a faint turbidity.

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[1] Compare Horbaczewski, Ztschr. physiol. Chem. **6**, 330.

The following table shows the average composition of the several dyspeptones studied:

	A.	B.	C.	D.	E.	F.	G.	Casein.
C	51.15	51.07	51.29	51.82	50.80	51.60	50.39	53.30
H	7.18	7.41	7.26	7.44	6.73	6.83	6.63	7.07
N	15.16	15.41	15.23	15.48	15.12	15.19	15.58	15.91
S	0.71	0.71	0.68	0.78	...	...	...	0.82
P	0	0	0	0	...	...	...	0.87
O	25.80	25.40	25.54	24.48	...	...	...	22.03
Ash	13.67	15.41	12.43	14.19	14.96	13.60	12.71	0.98

The ash was composed almost entirely of calcium phosphate, and the dyspeptones apparently contained no phosphorus whatever, other than that combined with calcium.

In the digestion of casein with pepsin-acid, the relative proportion of individual caseoses formed was found to depend somewhat upon the strength of the pepsin solution and the length of time the ferment was allowed to act. All of the caseoses are precipitable by saturation with ammonium sulphate. Proto-caseose, like the corresponding albumose, is precipitated from an aqueous solution by addition of rock-salt to saturation. Dry proto-caseose when moistened with water becomes immediately gummy and soon dissolves to a perfectly clear fluid, which on addition of considerable water becomes decidedly turbid. Treated with a large amount of water at the outset, it dissolves more slowly, giving a more or less cloudy fluid. In dilute acids and in dilute sodium carbonate it dissolves to a perfectly clear fluid. Towards heat, aqueous solutions of proto-caseose act exactly like proto-elastose. Even when warmed very gently, the solution becomes quickly turbid, and if concentrated, gives more or less of a precipitate. On cooling, the turbidity disappears, reappearing as the fluid is heated. Like proto-elastose also, a solution of the caseose body, on being rapidly concentrated, deposits more or less of the substance as a gummy mass, which, however, dissolves in cold water, or if the fluid is not too concentrated, dissolves in the mother-liquor as it cools.

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[1] Hoppe-Seyler's Med. chem. Untersuchungen, p. 463.

Two forms of deutero-caseose were obtained, called respectively α and β deutero-caseose. Both of these bodies stand much nearer to true peptone than proto-caseose, β-deutero especially so. α-deutero-caseose is partially precipitated from a salt-saturated fluid by a little acetic acid, and completely by saturation with ammonium sulphate in the cold; while β-deutero is precipitated as a sticky gum by ammonium sulphate, on boiling a solution saturated with the salt. The latter substance is especially characterised by a low content of carbon, and by its non-precipitation with acetic acid and potassium ferrocyanide, with nitric acid and with cupric sulphate. It stands unquestionably nearer to peptone than α-deutero, and is doubtless formed from the latter by the continued action of the ferment. α-deutero differs in its reactions from proto-caseose, especially in that it is quickly and completely soluble in water, and the solution when heated gives no coagulum whatever; also, in not giving any precipitate with either acetic or nitric acid. Bodies called hetero-caseose and dys-caseose were also formed, which resembled in many ways the corresponding albumoses. Further, by the action of dilute sulphuric acid at 100° C., and also by the action of the pancreatic ferment trypsin, caseoses of the same general nature as the preceding were formed.

On supersaturation of a digestive fluid with ammonium sulphate at 100° C., all of the preliminary products of proteolytic action are entirely removed, and in the present state of knowledge we assume as peptone any amorphous product of proteolytic action precipitable by alcohol and not precipitable by heating with ammonium sulphate added to saturation. With this fact in mind, casein antipeptone was formed by long-continued digestion of pure casein with alkaline solutions of trypsin, and then freed from all adhering proteoses. The purified peptones were found to be exceedingly gummy and excessively hygroscopic, requiring long-continued drying at 110° C. to remove the last traces of moisture. In reactions, they are characterised by extreme solubility in water, non-precipitation by nitric or acetic acid, by acetic acid and potassium ferrocyanide, by cupric sulphate, and by saturation with ammonium sulphate both in neutral and acid solutions. During the drying of the peptones at 110° C., prior to analysis, they apparently under-went a slight decomposition, indicated by the odor of valerianic acid; and likewise appeared to undergo a partial retrogressive metamorphism, inasmuch as after the drying, the preparations gave noticeable precipitates with nitric and acetic acids, and also by saturation with ammonium sulphate.

The composition of the casein antipeptones, and also of some of the caseoses, is shown in the following table:

		By Pepsin-acid.			By Trypsin.				
							Antipeptone.		
	Casein.	Proto-caseose.	α-deutero-caseose.	β-deutero-caseose.	α-deutero-caseose.	β-deutero-caseose.	A.	B.	C.
C	53.30	54.58	52.30	47.72	56.17	53.56	49.94	51.38	49.52
H	7.07	7.10	6.95	6.73	6.90	6.70	6.51	6.47	6.60
N	15.91	15.80	16.40	15.97	14.80	15.07	16.30	15.57	15.99
S	0.82	...	...	...	...	0.93	0.68	...	...

The researches of Kühne,[1] Hoppe-Seyler,[2] Weyl,[3] and Danilewsky[4] have shown that myosin, both from the animal and vegetable kingdom, is a globulin body, soluble in dilute sodium and ammonium chloride solutions, and precipitable therefrom either by the addition of salt in substance, or by dilution with much water. In spite of the interest attached to this peculiar proteid, little attention has been paid to its chemical nature since the time of its discovery by Kühne, and no attempt has hitherto been made to ascertain either its composition or whether the myosin obtainable from different animal sources is of the same chemical nature. Myosin was therefore prepared by extraction of thoroughly washed muscle-tissue from various sources, with either sodium or ammonium chloride solution (5–15 per cent.), and precipitation either by dilution with water or by dialysis until the salt was entirely removed. A large number of preparations were studied, thirteen of which were analysed, from ox, calf, sheep, fish, and other muscle, and showing such a close agreement that it is obvious that myosin as it occurs throughout the animal kingdom is a single chemical compound of constant composition. The average composition of all the preparations was as follows:

$$C\ 52.82,\quad H\ 7.11,\quad N\ 16.77,\quad S\ 1.27,\quad O\ 21.90,$$

being almost identical with the figures found by Hammarsten[5] for fibrinogen.

The coagulation point of an ammonium chloride solution of myosin was found to average about eleven degrees lower than a sodium chloride solution of the same strength, while a 5 per cent. sodium chloride extract of ox and sheep muscle grew turbid at about 57° C., and gave a flocculent precipitate at 63° C. Corresponding extracts of rabbit's, lamb's, calf's, and chicken muscle grew turbid at 52°–53° C., and gave a flocculent precipitate at 57°–62°

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[1] Protoplasma, Leipzig, 1864; also Lehrbuch der physiologische Chemie. [2] Handbuch der chem Analyse, **4** Auflage, p. 236. [3] Ztschr. physiol. Chem. Band **1**, p. 72. [4] Ibid, Band **5**, p 158.

[5] Jahresbericht der Thierchemie **10**, 11.

C. The results collectively fail to show the presence of a proteid coagulating at 47° C., given by Halliburton[1] as characteristic of myosin; but they do show a coagulum at about 56° C., corresponding to Halliburton's second proteid. Coagulums were also obtained at higher temperatures, showing an approach, at least, to the figures found by Halliburton in his fractional coagulation of salted muscle-plasma. Doubtless, myosin is formed, as suggested by Halliburton, by the interaction of one or more myosinogens and a ferment body.

Pure myosin was also digested with a solution of pepsin-hydrochloric acid, and its primary cleavage products studied and analysed. Proto and deuteromyosinose were obtained in considerable quantity; hetero and dysmyosinose only in small amount. The reactions of protomyosinose agree in general with those of protoalbumose, but with one important difference, viz., that an aqueous solution of the former free from salt, of whatever concentration, is not rendered turbid by nitric acid. Concentrated solution of sodium hydroxide, as in proto-elastose, produces a heavy, flocculent, gelatinous precipitate. Both proto and deuteromyosinose in aqueous solution react alkaline. In general, deuteromyosinose shows much the same reactions as the corresponding albumose, but is somewhat different from the latter, in that it is more difficultly precipitable. In composition, protomyosinose does not differ essentially from myosin, while deuteromyosinose contains a somewhat smaller percentage of carbon.

	C.	H.	N.	S.	O.
Myosin,	52.79	7.12	16.86	1.26	21.97
Protomyosinose,	52.43	7.17	16.92	1.32	22.16
Deuteromyosinose,	50.97	7.42	17.00	1.22	23.39

Myosin was found difficultly digestible in gastric juice, and the somewhat large residue of unaltered myosin was warmed for some days with a strong solution of trypsin, but still a large residue remained undissolved. The portion digested by the trypsin was found mainly as peptone, no myosinoses apparently being present.

Experiments on the physiological action of uranium salts are also recorded, as likewise the results of experiments on the influence of urethan, paraldehyde, antipyrin, and antifebrin on proteid metabolism. Uranium nitrate, from experiments on a large number of animals, is shown to be an irritant poison, producing gastro-intestinal irritation of more or less intensity. It is not in any sense a rapid poison, and the ingestion of a fatal dose of a uranium salt is not followed by any noticeable effect for some time; further, the action of a small amount (150 milligrams) is apparently as rapid and pronounced as that of large quantities (1 gram). The first noticeable symptom in rabbits is general weakness, lack of motor power, loss of co-ordination, and occasional temporary paralysis of the locomotor muscles. Introduced into the stomach in sufficient amounts, it checks digestion, and even stops it altogether. On the other hand, it appears to increase somewhat proteid metabolism, and also to increase the elimination of carbonic acid, and to raise the body temperature. Hence it is to be considered as having a direct action on nutrition, the disturbance of which is also plainly indicated by the rapid emaciation which follows the administration of uranium. It has a marked destructive action on the kidneys, causing an acute parenchymatous nephritis of the same kind as found in arsenic, mercury and phosphorus poisoning. Further, the large quantity of albumin found in the urine shows plainly that the blood-vessels are seriously involved in the inflammation. The albuminuria produced is severe and constant, and when the uranium is given in a single large dose, or in a small dose by hypodermic injection, albumin may appear in the urine within twenty-four hours. With small doses of uranium, the urine is decidedly increased in volume; but later on, when toxic action is more pronounced, there may be a partial or even complete suppression of the urine. The urine, too, in a short time after the administration of uranium, contains more or less sugar, but as a rule the sugar does not make its appearance until after the albumin. In the hypodermic injection of uranium, sugar appeared in a rabbit's urine within twenty-four hours. The production of glycosuria was found to be quite a characteristic symptom of uranium poisoning.

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[1] Journal of Physiology **8**, 133.

The influence of ethyl-urethan, antipyrin, and antifebrin on proteid metabolism, was studied by experiments upon healthy men, brought into a condition of nitrogenous equilibrium and fed upon a weighed diet of known composition throughout the experiment, which in each case extended over a month. The action of paraldehyde was studied in a similar way upon a large coach dog. The urine was analysed each day; in two of the experiments, total nitrogen, sulphur, and phosphorus were determined, while in the the other two, urea, uric acid, phosphoric acid, and chlorine were estimated.

The results obtained indicate that antipyrin has a decided inhibitory influence on the proteid metabolism of the healthy human organism, as shown by the diminished excretion of urea and uric acid when the drug was taken. Also, that antipyrin tends to diminish the volume of the urinary secretion. These conclusions are contrary to the recent results published by Kumagawa,[1] who found by experiments on a dog that antipyrin produced no change in the excretion of nitrogen, but did cause a noticeable increase in the excretion of uric acid.

Antifebrin or acetanilide in doses sufficiently large to produce an approach to cyanosis (214 grains in 7 days), gave rise to a slight increase in the excretion of urea; but as there was no corresponding increase in the excretion of either sulphur or phosphorus, it was not considered as having any very pronounced influence on proteid metabolism. On the excretion of uric acid, however, it appeared to exercise a special inhibitory influence.

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[1] Virchow's Archiv, Band **113**, 192.

Urethan was found to have a very decided diuretic action, and even in small doses greatly diminished the excretion of nitrogen. The excretion of sulphur was correspondingly diminished, but with small doses the excretion of phosphorus was apparently increased.

Paraldehyde, in the quantities given, had no special action on the excretion of either nitrogen, sulphur or phosphorus. Further, paraldehyde was found to increase somewhat the proteolytic action of pepsin-hydrochloric acid, but to have a very pronounced inhibitory influence on the amylolytic ferment of saliva. Antifebrin, even in very small quantities, checks the solvent power of saliva on starch, and also retards the action of pepsin. Antipyrin has only a very slight effect on the salivary ptyalin, but checks the action of pepsin; while urethan increases the amylolytic action of saliva, and retards only slightly the proteolytic action of pepsin.

Finally, we have space only to mention the experiments tried upon rabbits with soluble nickel and cobalt salts, with a view to studying the distribution of the absorbed poisons and their relative toxic action. The results collectively show that the two salts act very much alike, and that their poisonous action is somewhat slow, and manifested only when comparatively large amounts of the salts are administered. Both apparently cause death by stopping the action of the heart,[1] and also produce more or less disturbance in the alimentary tract, interfering with digestion, producing more or less inflammation of the mucous membrane of the stomach and intestine, and causing a more or less persistent diarrhœa. Both salts tend to produce a partial paralysis of the extremities, more pronounced possibly with cobalt than with nickel. They enter the circulation quickly, are rapidly distributed to all parts of the body, and are in turn more or less rapidly eliminated by the kidneys. Considerable, however, passes directly through the alimentary tract and is excreted with the faeces. The storage power of the individual organs is somewhat peculiar. The spinal cord and brain, in the majority of the experiments, stand first in their power of picking up and retaining the absorbed nickel and cobalt. This is in close accord with what has already been found with soluble forms of arsenic,[2] and more recently with strychnine[3] sulphate. Again, as with soluble forms of arsenic, the muscle-tissue retains a larger percentage of the metals than either the liver or kidneys. Another noticeable feature in the distribution of the absorbed poison is the comparatively large amounts retained by the lungs and heart.

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[1] See Blake, Amer. Jour. Science and Arts **7**, 194.

[2] This Journal **5**, 8, 12.

[3] Journal of Physiology **9**, 99.

BLAIR'S CHEMICAL ANALYSIS OF IRON.[1]

The term "technical analysis," as generally used, implies a short method which gives results of sufficient accuracy to serve as a guide in controlling a manufacturing operation. When, however, the chemical analysis is the basis on which ores or products are bought and sold, the most exacting demands are made on the chemist for the highest attainable accuracy.

From this standpoint, it is very interesting to follow the literature of the chemical analysis of iron for the last twenty-five years. The manufacture of steel by the Bessemer process had its foundation on the chemical determination of minute amounts of phosphorus in irons and iron ores; and the development to its present colossal proportions has only been made possible by the patient and exhaustive investigation of the composition of steel of different physical properties. But the steel-maker has not been content with mere accuracy. Owing to the great rapidity with which, in a modern steel plant, pig-iron is converted into steel ingots and these ingots into rails, the chemist has been compelled to devise shorter processes in order to keep pace with the work in the mill, and the result has been that there have been perfected in the chemical laboratories of iron and steel works methods which are marvels of rapidity and accuracy.

A book which should bring together an account of the principal modern methods for the chemical analysis of iron ores, pig-iron, steel, and the materials used in iron and steel making, has long been needed. Troilius's *Notes on the Chemistry of Iron* is excellent as far as it goes, but its scope is limited. Jüptner von Jornstorff's *Praktisches Handbuch für Eisenhütten-Chemiker* is probably the best book devoted entirely to this subject, but it is not accessible to chemists without a knowledge of German. It will be, without doubt, generally admitted that the person best qualified in this country to write a book on chemical methods of iron analysis is Mr. Blair. His long experience in work of this kind, both in his private practice and as chemist of the United States Board appointed to test iron, steel and other metals in 1875, and of the United States Geological Survey, and the Tenth Census, has made him the first authority on this subject. It is therefore a matter of congratulation for all chemists that Mr. Blair has taken the time from a busy professional life to write a work which might otherwise have been undertaken by a less competent hand.

The compilation of the best methods now in use has been well done, and, in some cases, Mr. Blair has had contributions prepared specially for this book, from chemists of steel works, describing their own methods. But the great value of the book will be found, we think, in the detailed description of processes as carried out by Mr. Blair in his own practice. Uniformity of treatment and manipulation is necessary often to ensure agreeing results; the mere outline of a process will often mislead. The patience with which Mr. Blair has, in many cases, given each step of the process as he performs it, is much to be commended.

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[1] The Chemical Analysis of Iron: A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace and producer gases. By Andrew Alexander Blair. Philadelphia: J. B. Lippincott Company, 1888.

We could wish that Mr. Blair, in describing various methods for the determination of the same element, had permitted himself the privilege of criticism and comparison of the methods as regards accuracy and simplicity of working. A beginner who goes to the book to find the best method for determining a certain element may find himself embarrassed by the choice presented to him. This is notably the case in regard to carbon. All the processes which have ever been proposed for the determination of total carbon in iron are here admirably classified, but the reader is not informed that some of these processes have fallen into disuse either because inaccurate or because there are simpler ones available.

In the chapter on the determination of metallic iron in iron ores there is a singular omission to mention the use of mercuric chloride to convert into stannic chloride any excess of stannous chloride which may have been used in the reduction of the ferric chloride. This is by far the simplest and most perfect of all the methods in use for the reduction of ferric salts previous to titration. It has long been in use for the bichromate method, and has recently been adapted to the use of permanganate, by the addition of manganous sulphate to the solution. Pulverised zinc should also have had mention as a more convenient agent for reducing ferric solutions than granulated zinc.

In fusions with alkaline carbonates and nitre for the determination of sulphur, Mr. Blair implies that the only danger of the sulphur in the gas being absorbed by the fusing mixture is when the mass overflows the outside of the crucible. We think most chemists will not agree with him on this point. An appreciable absorption of sulphur from the gas by the fused mass in the crucible has been noted when the fusion lasts fifteen minutes or more. Fusion in a gas muffle is accompanied by much less contamination with sulphur than when the crucible is heated over the free flame, but an alcohol lamp is, in all cases, to be preferred for fusions for sulphur. The apparatus described in the book, many of which are original with Mr. Blair, are characterised by fitness and simplicity, and the cuts of them are models of clearness. The book is also to be praised for admirable typography and good paper. But we cannot help thinking that the fair page is marred by the general use of chemical symbols for abbreviations. This practice is objectionable from any point of view, and we cannot think why the author adopted it, unless it was to save space. For our part we should have preferred the book in greater bulk rather than to read " HCl " in place of "hydrochloric acid."

In connection with the thorough modern character of the book as regards methods, it is interesting to observe the conservatism of the author in clinging to the older nomenclature. "Acetate of sodium and carbonate of calcium" look strangely in a modern chemical book. Occasionally the author is off his guard and there slips in the more recent form, giving a rather droll effect, as when "cupric chloride" and "sulphate of copper" stand side by side. But these are not serious blemishes.

The table of atomic weights is not fully abreast of the latest research, and might be advantageously revised in a future edition.

Mr. Blair says, in his preface, that the work "is intended to be a guide for the student of iron chemistry only." The book is sure of a warm welcome from the chemists of iron works, but, if we mistake not, it will have an equally cordial reception from teachers of chemistry, many of whom lack an intimate knowledge of the chemical practice of iron and steel works.

T. M. DROWN.

NOTES.

A New Technical Method of Preparation and a Partial Synthesis of Cocaine.

The cocaine extracted from coca leaves contains a number of other alkaloids from which it must be separated. These alkaloids have hitherto been of no value, and their presence has only interfered with the preparation of cocaine. C. Liebermann and F. Giesel[1] have recently shown that by boiling the alkaloids for an hour with hydrochloric acid they are all converted into ecgonine. They have further succeeded in devising a method for converting ecgonine into the benzoyl derivative, and benzoyl-ecgonine can, finally, be converted into methyl-benzoyl-ecgonine or cocaine by the method of Einhorn. The preparation of benzoyl-ecgonine is effected by digesting ecgonine, water, and benzoic anhydride on a water-bath. It is thus possible to convert a very considerable quantity of otherwise worthless compounds into the valuable cocaine. I. R.

An Attachment for Stirrers Used in Determining Melting Points.

To obviate the ordinary difficulties met with in stirring the liquid of the bath used in determining melting points, the apparatus described below has been devised. The attachment for the stirrer consists of a spiral about eight inches long and threeeighths of an inch in diameter, made by coiling a wire around a glass rod or tube.

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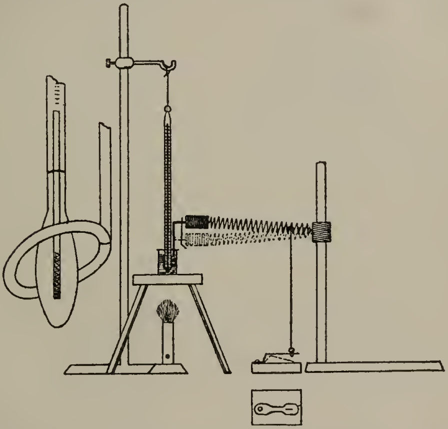
[1] Ber. d. chem. Gesell. **21**, 3196.

The wire should be stiff enough to support a small glass stirrer at one end, and yet not so stiff as to prevent it from oscillating readily when gently touched. At one end of the spiral the wire is coiled around a small cork, which is perforated to receive the handle of the small glass stirrer. The other end of the spiral is firmly attached to a larger cork, which is perforated so as to fit tightly the upright rod of a lamp-stand. A spring about two and three-quarter inches long, made from a thin strip of brass by cutting and bending to the form shown in the figure, is screwed to a small wooden block. About half an inch from the free end is soldered a small hook made of copper wire. This hook is connected by means of a light wire with the spiral above.



In setting up the apparatus, the cork should be arranged on the lamp-stand so as to bring the loop of the stirrer just under the surface of the liquid in the beaker when the spring is at rest. The press-spring should be as light as practicable, so as to offer the minimum resistance, and the block carrying it should be weighted or screwed to the desk, to avoid displacement while stirring.

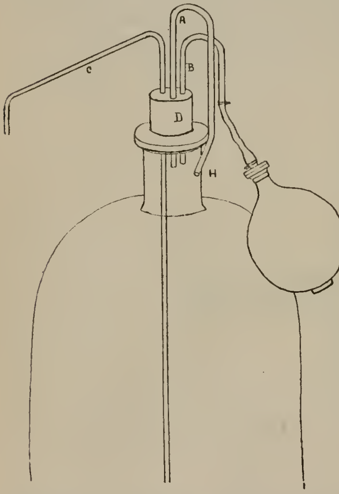
If the wire connecting the hook with the spiral is attached to the latter two inches from the fixed end, when the press-spring is moved downward a quarter of an inch by means of the forefinger, the stirrer will have a one-inch stroke. On removing the finger, the spiral spring carries the stirrer back to the original position. By the use of this apparatus the temperature of the liquid is kept uniform, and the investigator is enabled to put the whole of his attention on the thermometer and the substance being melted, while his forefinger operates the stirrer without becoming wearied.

Edward C. Holton.

Mass. Inst. Tech., Boston, *March*, 1888.

A Simple Acid-Pump.

Although this device, in slightly different forms, has been in use for some time, yet the convenience of the modification here figured may render it worthy of description.



A, *B* and *C* are three glass tubes passing through the rubber stopper *D*, *A* and *B* ending just below the stopper, and *C* reaching to the bottom of the bottle. To *B* is attached a double-valve rubber bulb. *A* is so bent that, while the bulb is clasped in the hand, the thumb can easily be held over the open end of *A* at *H*. Acid can then be forced out through *C*, and the flow may be checked instantly by removing the thumb from *H*. The left hand is thus left free to hold under *C* the vessel into which the acid is to flow. A glazed earthenware dish is placed upon the table under *C* to catch the drippings.

For the use of large classes of beginners in general chemistry this apparatus is well adapted, since accidents resulting from careless handling are rendered almost impossible, and both acid and time are economised.

The same device may be used for carboys, the tube *C* being extended upwards so that an acid bottle may stand on the box beneath it, and *H* being kept closed by a piece of rubber tubing and a pinch-cock.

L. M. Dennis.

Chemical Laboratory, Cornell University.

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ON THE CRYSTAL FORM OF METALLIC ZINC.

By Geo. H. Williams and Wm. M. Burton.

Of the crystal form of metallic zinc very little is definitely known. This element is generally regarded as hexagonal, and as probably isomorphous with the rhombohedral metals, arsenic, antimony, bismuth, and tellurium, but the basis of observation upon which such statements rest is extremely meagre. The production of remarkably perfect crystals of zinc, in the course of the determination, by one of the writers, of its atomic weight,[1] seems therefore of sufficient interest to warrant their study and description.

With the exception of certain casual and inaccurate statements by Berzelius, Berthier, and Laurent, the first account of zinc crystals was given by Nöggerath in 1836, who obtained them as the accidental product of a furnace near Lüttich. He describes them as hexagonal prisms, often barrel-shaped like corundum, and strongly striated parallel to the base.[2] G. Rose subsequently attempted to measure these crystals, but with only partial success. One crystal gave him in three consecutive zones, as the inclination of a pyramid to the basal pinacoid, the values 110° 35′–50′, 110° 31′–42′, 111° 45′–50′;[3] which are, so far as we can ascertain, the only measurements on zinc crystals which have heretofore been published. In 1848 Nicklès described crystals of zinc obtained by Favre while distilling the metal in an atmosphere of hydrogen, and considered them as pentagonal dodecahedrons,[1] but these forms Rose afterwards showed to be irregular polyhedral aggregates without symmetry.[2] Further observations have been made on the hexagonal form of zinc by Stolba, but these are unsupported by measurements.[3] In various alloys zinc is known to assume a regular form,[4] but in the pure state it is known only as hexagonal.

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[1] H. N. Morse and W. M. Burton: The atomic weight of zinc as determined by the composition of the oxide. This Journal **10**, 311.

[2] Krystallform des regulinischen Zinks. Ann. der Phys. Pogg. **39**, 223.

[3] Ann. der Phys. Pogg. **83**, 129, and Monatsber. Berl. Ak. Juli, 1850.

The absolute purity of the zinc obtained by successive distillations in a vacuum has been described by Morse and Burton (loc. cit.) Careful analysis disclosed no trace of any other substance, nor could any be discovered with Rowland's 20-foot concave grating spectroscope.

By the ordinary rapid distillation which took place in a horizontal glass tube placed in a combustion furnace, the zinc formed in globules on the top of the tube, and as these increased in size they dropped down, forming a solid bar of metal. The larger of the globules which remained on the upper portion of the tube when it was cooled became bounded by a multitude of bright plane surfaces; the smaller of these globules, when examined with a lens, were found to have formed minute barrel-shaped crystals terminated by a hexagonal basal plane, parallel to which their sides were finely striated.

Examination showed that neither of these varieties of crystals were suited for accurate measurement, and an attempt was therefore made by much slower distillation at a lower temperature to secure more perfect ones. Different parts of the tube were unequally heated, and kept for several hours at a temperature not far from the melting point of the metal. This attempt proved successful. Three different types of crystals were formed: spheroidal polyhedral aggregates, barrel-shaped crystals, and tabular hexagonal plates. Although the last named alone furnished crystallographic data, it will be of interest to describe each type.

Polyhedral Aggregates.—The larger globules which remain on the upper surface of the tube vary between one and eight millimeters in diameter, and become upon cooling what seem to be at first glance brilliant but very complicated crystals. They are bounded by a multitude of planes, but a more careful examination shows that these are without symmetry of arrangement. Indeed, in no two is the arrangement the same. Fig. 1 shows an unusually simple form of this kind 4 mm. in diameter and 2½ mm. high, and Fig. 2 gives the projection of its faces on a plane surface. As a rule, however, these forms are more nearly spherical in shape, and bounded by a much greater number of planes. They are evidently what Nicklès mistook for pentagonal dodecahedrons, and in fact the planes frequently have a pentagonal shape. In reality they are, as G. Rose showed, complicated aggregates of crystals, similar to those formed by the cooling of a globule of pyromorphite after it has been fused before the blow-pipe. The fact of their aggregate structure is often well shown by the presence of finely striated surfaces, the striations running in many different directions, while in simple crystals they are always parallel to the basal plane. These aggregates are not entirely bounded by planes. Between these, curved surfaces of greater or less extent frequently occur, as shown in the figures.

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[1] Sur la forme cristalline du zinc métallique. Ann. chim. phys. (3) **22**, 37, 1848.

[2] Ann. der Phys. Pogg. **85**, 293, 1852.

[3] J. prakt. Chem. **96**, 182, 1866.

[4] Rose: Ueber die Dimorphie des Zinks: Ann. der Phys. Pogg. **107**, 448, 1859. J. Cooke: Am. Jour. Science (2) **31**, 194, 1861; vid. also Rammelsberg: Handbuch d. krystallographisch-physikalischen Chemie **1**, 186. 1881.

Barrel-shaped Crystals.—The general character of these is shown in Fig. 3. They are always minute, never exceeding two millimeters in diameter. Their bases are sharply defined and hexagonal, but their sides are finely striated. It can also be seen under the microscope that these striations are not absolutely parallel, indicating that the little plates of which the crystal appears to be built up do not have their vertical axes in exactly the same line. On the reflecting goniometer these barrel-shaped crystals give a continuous " shimmer " reflex between planes inclined about 140° to the two basal pinacoids. There are indeed points in this continuous light band where the reflection is brighter than at others, but the examination of a number of crystals convinced us that they were unevenly distributed and unreliable. The brightest point, however, invariably occurred after a revolution of about 57° from the basal plane, indicating the position of the fundamental pyramid.

Tabular Crystals.—The third type of crystals, having a tabular habit, were produced only when the distillation of the zinc proceeded slowly and at a moderate temperature. These are more perfect and simpler in their crystal form, and are the only ones whose planes allowed of satisfactory measurement. Even these smallest and thinnest crystals are shown by the microscope to be composed of piles of sharp hexagonal plates whose boundaries are parallel but not coincident. Rapid alteration in the size of these plates may produce very irregularly shaped crystals, as shown in Fig. 5. There is, however, an average decrease in their size as the pile grows upward, producing a gradation of the tabular into the barrel-shaped crystals. This method of superposition is represented in Fig. 6. The fact that the angles of these little hexagonal plates do not lie in the same line, although their sides are parallel, often produces a rough edge between the adjoining pyramidal faces. This projection of the hexagonal angles of the successive plates may form a pseudo-plane of the second order, as shown in Fig. 7. True planes of the second order also occur as truncations on one or more of the polar edges of the pyramids (see Figs. 3, 4, and 5), but these are very minute and more or less curved.

A series of measurements was made with the revolving stage of a microscope, for the purpose of detecting any possible variation in the plane angles of the hexagonal plates from 120°. The sharp boundaries allowed of very accurate adjustment, but no such disagreement could be discovered. The angles varied on either side of 120° only within the limit of the error of observation.

For purposes of exact measurement, small crystals of tabular habit (one millimeter or less in diameter) were alone found to be serviceable. Out of a large mass of these, only a few were found to be satisfactory, even when examined with a pocket lens; and of those thus selected, by no means all yielded results upon the goniometer. After carefully testing a number of crystals, seven were finally chosen as giving reflections which were sharp enough to be considered reliable. Each of these was measured in as many zones as possible, but it was only seldom the case that more than 90° could be measured from the base, as one-half the crystal was usually much less perfect than the other.

The strongest, though not in all cases the sharpest, reflection was obtained from a pyramidal plane whose inclination to the basal pinacoid was approximately 123°. This was, therefore, assumed as the unit pyramid. Three of the sharpest images were obtained at 122° 32′, 122°.33′ and 122° 33′; and as the angle 122° 33′ 24″ was obtained as the mean of all the measurements made upon the five crystals (yielding a total of eighteen zones) upon which this form was identified, this was taken as the basis for calculating the axial ratio, $a : c = 1 : 1.356425$.

The mean of five measurements of the polar angles of this same pyramid, made on three different crystals, gave 130° 20′, corresponding to the ratio $a:c = 1:1.3493$, but this may be regarded as less accurate than that first given.

The following is the table of angles measured on seven different crystals with a horizontal goniometer (Fuess's Model 2). The inclination is given in each case of the respective pyramidal plane to the basal pinacoid. When more than one zone was measured on a single crystal, the mean result is stated, and the number of zones upon which this average is based is given in parenthesis. The reflections of the signal were by no means all that could be desired, being sometimes broad, sometimes compound, and sometimes very faint. The sharpest image was given by the basal plane, and the next best by the fundamental pyramid. Very indefinite reflections were discarded, and it is believed that the results are as good as could be secured with the material at hand. In but few cases did the differences in similar angles reach a degree; for the most part they were far within this limit.

The required angles are calculated for the axial ratio, $a:c = 1:1.356425$.

Crystal.	$\frac{4}{7}$P.	$\frac{2}{3}$P.	P.
I.	138° 11′ (1)	...	...
II.	138 41 (2)	133° 24′ (3)	122° 32′ (3)
III.	...	134 00 (1)	122 34 (3)
IV.	...	...	122 47 (4)
V.	138 00 (1)	133 15 (1)	122 18 (4)
VI.	...	...	...
VII.	138 45 (2)	133 07 (3)	122 36 (4)
Mean,	138 24	133 27	122 33 24″
Calculated,	138 10	133 46	...
Difference,	+ 14′	— 19′	...

Crystal.	$\frac{3}{2}$P.	6P.	∞P.
I.	...	...	...
II.	...	95° 57′ (2)	89° 58′ (1)
III.	...	...	...
IV.	113° 18′ (1)	...	90 08 (1)
V.	...	96 42 (1)	90 08 (2)
VI.	112 34 (1)	96 15 (1)	...
VII.	114 05 (1)	96 10 (1)	90 04 (5)

	$\frac{3}{2}$P.	6P.	∞P.
Mean,	113° 19′	96° 18′	90° 05′
Calculated,	113 03	96 04	90 00
Difference,	+ 16′	+ 14′	+ 5′

No other angles were measured except the polar angles of the form P, which gave, as above stated, 130° 20′ as the mean of five determinations on three different crystals. An attempt was made to locate the pyramid of the second order, whose little plane on some of the crystals appeared quite brilliant. This was, however, unsuccessful. This face when best developed is curved and gives no reflex of the signal, while its minute size renders its accurate centering difficult. In one case (Crystal II), a reading of 117° 17′ was made as the inclination of this face to the basal plane, but it was accomplished without the signal, and cannot be regarded as satisfactory.

A large number of other pyramids of the first order undoubtedly exist, as is indicated by the almost continuous "shimmer" obtained from the barrel-shaped crystals, as well as by many faint reflections of the signal at points intermediate between the values given in the above table. In a single zone of Crystal II, the following series of readings lying between the forms $\frac{3}{2}$P and 6P was made from reflections of the signal, which, though faint, were fairly well defined: 104° 10′, 103° 19′, 100° 56′, 98° 42′.

These yield the symbols for four additional pyramids as follows:

	$\frac{5}{2}$P.	$\frac{8}{3}$P.	4P.	$\frac{13}{3}$P.
Observed,	104° 10′	103° 19′	100° 56′	98° 42′
Calculated,	104 20	103 28	101 04	98 23
Difference,	— 10′	—9′	— 8′	+ 19′

Inasmuch, however, as it was possible to identify these pyramids only in one zone of a single crystal, they cannot be regarded as so characteristic as those planes found to occur in different zones of several crystals. No reflection corresponding to the angles given by Rose was observed on any of our crystals.

At first glance there is nothing about the distribution of the planes on the zinc crystals to indicate a rhombohedral character. Surely the unit pyramid (P) occurs with a holohedral development, as its presence was determined three times in four consecutive zones, and twice in three. Nor could any regularity be observed in the absence of the more obtuse pyramids $\frac{4}{7}$P and $\frac{2}{3}$P, for they were often present in two consecutive zones, while they were wanting in others. The two acute pyramids $\frac{3}{2}$P and 6P were, however, in several instances observed to alternate with each other, as well in consecutive zones as on opposite sides of the prism in the same zone. This indicates a rhombohedral development of these forms, and as such they are represented on the ideal restoration of a tabular zinc crystal, Fig. 8.

Cohesion Phenomena.—As is well known, the cleavage of metallic zinc is very perfect parallel to the basal pinacoid. Brilliant cleavage surfaces could be readily obtained by splitting the little crystals with a knife-blade. No trace of any rhombohedral cleavage could be discovered. Rose observed that basal cleavage surfaces were frequently striated in three directions parallel to what he considered the faces of the rhombohedron. Similar striations were also observed intersecting at angles of 60°, but they were found to be pressure lines produced by cleaving the metal. Experiments were made with striking the point of a fine needle into the basal plane or cleavage surface, when a six-rayed star was produced, composed of systems of fine lines which were parallel to the boundaries of the crystal as well as to the pressure lines. The direction of these rays corresponds to those of the percussion figure (Schlagfigur) in mica, as shown in Fig. 9. Similar results were also obtained with bismuth and graphite. Attempts to produce secondary twinning lamellae by subjecting the zinc crystals to pressure were unavailing, as were also efforts to establish their symmetry by etching.

Relation to the Rhombohedral Metals.—Since the work of Rose, zinc has been regarded as rhombohedral, and as isomorphous with the elements arsenic, antimony, bismuth, and tellurium.[1] The axial ratio obtained from Rose's measurements, 2.177, does not, however, accord well with this assumption. The result obtained from our unit pyramid, on the other hand, agrees very closely with the ratios of these other metals.

Arsenic, 1 : 1.4025, Zepharovich (Sitzungsber. Wien. Ak. Vol. 71, 1875).
Antimony, 1 : 1.3236, Laspeyres (Zeitschr. deutsch. geol. Gesell. 1875).
Bismuth, 1 : 1.3035, Rose (Abh. Berl. Ak. 1849).
Tellurium, 1 : 1.3298, Rose (ibid.).
Zinc, 1 : 1.356425, Williams and Burton.

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[1] Ueber die Krystallform der rhomboëdrischen Metalle, etc. Abhandlungen der Akad. der Wiss. in Berlin, 1849, p. 73.

The cleavage of zinc agrees with that of all except tellurium, but the habit of the crystals, in spite of the similarity in axial ratio, is altogether different. This may, however, also be said of the other members of this group.

The zinc crystals measured by us cannot be said to definitely show the rhombohedral character of the metal. Nevertheless, analogy indicates this; and on the supposition that the positive and negative rhombohedrons of the same symbol occur in equal development, there is nothing in the form of the hexagonal pyramids which is positively opposed to it.

Certain striking points of resemblance may be noticed between the crystallisation of zinc and the hexagonal and pseudo-hexagonal members of the chlorite group, chlorite, pennine, and ripidolite. Here, as in the case of all the approximately hexagonal minerals possessing a very perfect basal cleavage, like mica, graphite, or molybdanite, it is only under the most favorable possible conditions that the lateral planes are sufficiently well developed to allow of accurate determination. Moreover, the absence of those delicate optical tests which have done so much to establish slight variations from hexagonal symmetry in transparent minerals like mica, must ever leave the true nature of opaque crystals of the same habit in doubt.

EXPLANATION OF THE PLATES.

Plate I.

Fig. 1.—View from the side of a comparatively simple polyhedral aggregate of zinc, 2½x4 mm.

Fig. 2.—Projection of the same upon a plane passed through its center, showing curved surfaces between the planes.

Fig. 3.—Barrel-shaped crystal, 1½ mm. in diameter, with irregular edges between its pyramid planes, and indications of forms of the second order.

Fig. 4.—Thick tabular crystal, showing pyramid of the second order, generally curved.

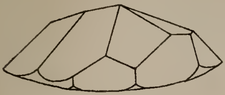
Fig. 5.—Irregularly shaped crystal produced by the superposition of plates of unequal size.

Plate II.

Fig. 6.—Superposition of hexagonal plates of different size.

Fig. 7.—Diagram representing a tabular crystal composed of

1



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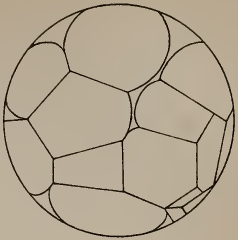

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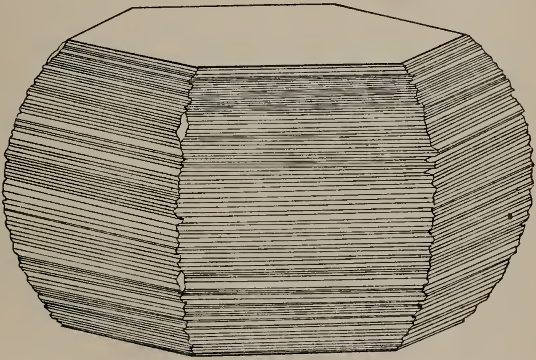

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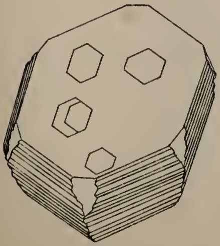

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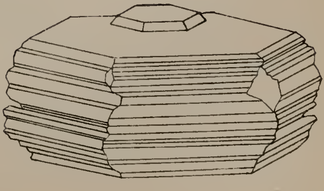

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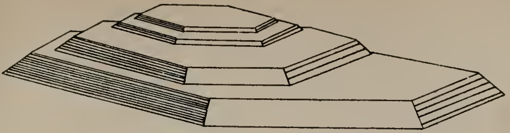

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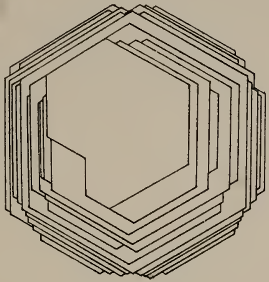

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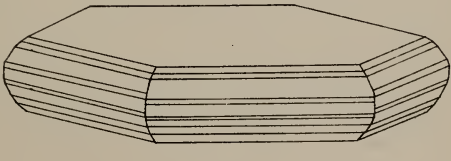

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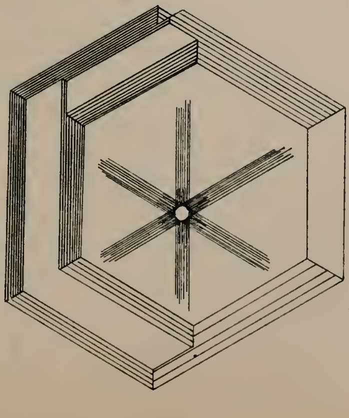

J.H.W. del.

superposed plates whose sides are parallel, but whose angles produce a pseudo-plane of the second order.

Fig. 8.—Ideal development of a tabular zinc crystal, showing the forms OP, $\frac{4}{7}$P, $\frac{2}{3}$P, P, $\frac{3}{2}$P (rhombohedral [?]), 6P (rhombohedral [?]), and ∞P.

Fig. 9.—Six-rayed star (percussion figure) produced by the point of a fine needle.

Contributions from the Laboratory of the United States Department of Agriculture.

XI.—BORACIC ACID AS A PLANT CONSTITUENT.

By C. A. Crampton.

In the year 1887 I examined 36 samples of wine, obtained in the local market, for adulterations. In applying a test for boracic acid to these samples, I was surprised to find that all but two gave a distinct test for this element. It did not seem possible that it could have been added to the wines for purposes of preservation, for it could hardly have obtained so extensive a use for this purpose; and, besides, in many cases I found other preservatives present, salicylic acid and sulphurous acid, which are much more efficient for this purpose than borax. Yet I did not feel justified in concluding that it was a normal constituent of the wine, for my samples were not such as could be properly used as the basis of such an assumption. In fact, I was at a loss to account for the matter, and passed it over in the Bulletin referred to,[1] expecting to give it further attention at a later period. Baumert[2] had already published an article giving the results of a very thorough examination made by him upon some California wines. He had the same experience I did in making his tests for boracic acid, finding it in every sample he examined. He was loth to believe that it could have found so extensive a use as a preservative, and ventured the hypothesis that it had been taken up by the plant from the soil, knowing that some California soils contain borax. But his samples were only 8 in number, and all came from California. My samples came from various parts of the United

[1] Bulletin No. **13**, Part III, U. S. Department of Agriculture, Chemical Division, p. 363.

[2] Landw. Vers. Stat. **33**, 39.

States, including California, and I obtained the test in wines from places as widely distant from one another as New York, Ohio, North Carolina, and Virginia. So the acceptance of the hypothesis that it was derived from the soil would necessarily imply that the soils of all these localities contained boracic acid as one of their constituents, and I hesitated about deciding that such was the case from the small amount of evidence at hand. In the meantime, Professor Rising, of California, stimulated to the defense of the purity of the natural wines of his State from the implication cast upon them by Baumert's and my analyses, set himself to the task of proving that boracic acid was a normal constituent of natural grape juice. The following extract from a letter he sent to me in July, 1888,[1] shows the results of his work. He says:

"We have proved beyond any question, I think, the presence of boracic acid in many unadulterated California wines. In addition to the test with turmeric paper, we have obtained the flame test so decided that there can be no doubt. I have just received a new spectroscope, and I shall hope by its aid to settle this point beyond all question. Our method of work is as follows: 50 to 100 cubic centimeters of wine are evaporated in a platinum dish, ignited and burned to ash. Part of this ash is transferred to a platinum spoon; such an one as is used for blow-pipe work answers very well. A few drops of the strongest H_2SO_4 (I have used a 96–98 per cent. acid), then alcohol, is added, and then lighted and immediately blown out, and relighted and again extinguished. The first flash will show the acid very distinctly if it is present."

Thus the fact may be said to be established that boracic acid is a normal constituent of *California* grapes. But others have made investigations on this point, and abundant evidence has been obtained to the effect that it is to be found in wines in many different parts of the world. Baumert gives, in a recent number of the *Berichte*,[2] the results obtained by himself and others in this direction. Soltsien[3] concluded, from the observations of himself and others, that boracic acid was not an unusual constituent of wine ash. Ripper[4] found it as a normal constituent not only of 1000 different samples, including both German and foreign wines, but also of various parts of different grape stocks. He also succeeded in isolating it as fluoborate of potassium from 2 liters of a Riesling wine. Baumert himself says he has made it a practice for the last three years to test every wine that came into his hands for boracic acid, and found it present in every case without exception! These samples included German, Spanish and French wines, also wines from grapes grown in Saxony, Thuringia, and musts from Freyburg and Naumburg. He also tested for it in all parts of grape-vines grown near Halle—in the leaves, wood, fruit, stems, etc.—without failing to obtain positive results in any case. Soltsien[1] obtained like results on the so-called wild grape-vine (*Ampelopsis quinquefolia*).

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[1] Published in full in Bulletin No. **19**, Chem. Div. U. S. Dept. Agriculture, p. 38.

[2] **21**, 3290.

[3] Pharmaceutische Zeitung **33**, 312.

[4] Weinbau und Weinhandel; Organ des Deutschen Weinbau Vereins, No. **36**, 1888.

There can no longer be any question, therefore, in view of this mass of evidence, that boracic acid is a normal and frequently occurring constituent of the grape plant; and that this is true not only as regards wines grown in any particular section, but holds good of a considerable part of Europe and of the United States. The peculiar part of my own analyses now seems to be that I found any samples which did *not* give the test. (There were two wines among those I examined in which I could get no test for boracic acid; both were Catawba wines; one was made in Pleasant Valley, N. Y., the other in Bass Island, a small island in Lake Erie, northeast of Toledo.)

If boracic acid is so universal a constituent of the grape plant, why not of other plants as well? This occurred to me as soon as I saw the articles containing the results of the work of the European chemists upon the grape-vine, and I immediately proceeded to apply the test to all the samples of plant-ash we had on hand in the laboratory. Mr. A. E. Knorr, of this department, has been engaged lately in the prosecution of the chemical part of an inquiry into the disease known as the "yellows" in peach trees. In the course of his work he had occasion to make analyses of the ash of various parts of the peach trees, portions of which he still had on hand. At my suggestion he applied the turmeric paper test to all these samples, and the result was to show the presence of boracic acid in each and every case. The samples included ash from the following parts of the plant: leaves, stems, wood, and fruit, including kernels. I then applied the test to all the plant ashes I could find in the laboratory, with the following results:

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[1] Phar. Zeit. **33**, No. 90.

Thirteen different samples of ash from various parts of the fruit of the watermelon vine gave good tests in every case. These included every part of the fruit: rind, pulp, juice and seed, and were obtained from watermelons purchased in Washington, D. C.

A sample of ash from apples gave no test.

A sample of ash from sugar-beets grown in Oregon gave no test.

A sample of ash from southern sugar-cane grown in Louisiana gave no test.

In connection with the results of the test on ash from apples, I would say that all the samples of cider (12) included in my investigation, published in Part III, Bulletin No. 13, were subjected to the test for borax, with negative results in each case.

From the results of these few tests it is evident that the occurrence of boracic acid as a constituent of plants is much more general than has been supposed. If it is found so constantly in grape juice in different parts of the world, and in such dissimilar plants as the peach tree and the watermelon vine, I have no doubt but that it will be found in a great many other plants, now that the attention of chemists has been called to the matter. No analysis of plant-ash will be complete in the future without a search for this constituent. I hope to be able soon to make a quantitative estimation of it in some of the samples I have on hand.

Considering the fact of the relatively small number of mineral substances found in plants, and the importance which has been accorded them in chemical science, it seems strange that the occurrence of this element has remained so long unknown. In the brief search I have been able to make in chemical literature I can find no mention of its being found as a constituent of plants. It must be derived from the soil, of course, but none of the authorities I have consulted speak of its occurrence outside of the localities where it is in sufficient quantities to constitute a mineral deposit and a commercial source of supply. Hilgard[1] speaks of its occurring in the so-called alkali soils of California, but these might be included in the above category, as it is from similar sources that all our supply of borax in this country is drawn.

Baumert[2] could obtain no test in a specimen of soil taken from a wine-growing district in California. Doubtless the test would be more difficult to obtain from a soil than from the ash of the plant grown upon it, as the salt would be accumulated in the latter.[1] Spectroscopic examination would probably prove useful in the case of soils. In my experience, the test for boracic acid by means of the peculiar red color imparted to turmeric paper is fully as delicate as the flame test and much more satisfactory. I obtained the former in many cases where I could not get the latter satisfactorily, and I have found difficulty in getting the greenish flame where I made tests upon known but small quantities of borax. The turmeric test is not only delicate but very distinctive, the only salt giving a coloration which could possibly be mistaken for it being ferric chloride, and the brownish color produced by this does not very closely resemble the characteristic reddish color produced by boracic acid, and, moreover, does not undergo the change to greenish black on dipping into an alkali solution which is developed in the latter. Baumert[2] relies upon this test, and considers the precautions superfluous which Ripper and Soltsien observed in its application.

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[1] 10th U. S. Census Report.

[2] Landw. Ver. Stat. 33, 87.

The instances where I failed to obtain a test in some of the ashes examined show either that this element is not universally distributed in all soils, or that some plants have a selective affinity for it, absorbing it from all soils while other plants reject it. The latter would seem to be the more probable hypothesis from the evidence we have at present, but further investigations will be necessary to establish this point.[3] It is a most interesting subject, and I hope we will soon have further light thrown upon it. Aside from the interest which attaches to its occurrence *per se*, its relation to the examination of food materials for artificial preservatives which have been fraudulently added, makes it a matter of direct practical importance. Boracic acid shares with salicylic acid, sulphites, hydronaphthol, etc., the distinction of being used for such purposes, and until we have more definite information as to the extent and limits of its existence as a normal constituent of vegetable matter, we cannot rely, as heretofore, upon a mere qualitative proof of its presence in a food material, such as wine, canned goods, etc., as an indication of fraud in the preparation of the material examined.

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[1] It is interesting to note in this connection the surprisingly large percentage of boron found by Messrs. Gooch and Whitfield in mineral waters from the Yellowstone Park (Bull. No. 47, U. S. Geological Survey). They found it present in nearly all of the samples examined, and in some cases to the extent of nearly 3 per cent. of the total solid matter. These waters are of course peculiar in their origin, but perhaps a search for this element in water analysis in general would develop a more extensive distribution of it than has been heretofore supposed. I doubt if a test for it is often included in an ordinary water analysis.

[2] Op. cit. p. 3291.

[3] Prof. F. W. Clarke, of the U. S. Geological Survey, has suggested to me that perhaps a study of the origin of the soil upon which boron-bearing plants grew would have some bearing upon the subject of the distribution of this element. His idea was that soils of granitic origin would be likely to contain it, while those derived from the disintegration of limestone formations might not, and he called my attention to the fact that both the wines in which I was unable to prove its presence were from limestone districts. Prof. Clarke also reminded me of the volatilisation of boracic acid when an alcoholic solution of it is evaporated, and suggested the precaution, which I would recommend to chemists, of fixing the acid by the addition of an alkali when making the test in wines, so that no trace would be allowed to escape.

XII.—SPECIFIC GRAVITY OF SOME FATS AND OILS.

By C. A. Crampton.

During the investigation of fats and oils made in this laboratory the past year, the results of which will shortly be issued as Part IV, Bull. No. **13**, Chemical Division, I had occasion to determine the specific gravity of the large series of samples examined. This was done by means of the Archimedian method, as recommended by Allen,[1] using the plummet of a Westphal balance, but making the weighings with an ordinary balance. The plummet was ground to displace 5 grams of pure water at a temperature of + 35° C. The method gave very good results, and was easy and rapid in its execution—a very desirable condition, in view of the large number of samples. Some of the fats, however, were solid at 35°, and their densities could not be determined in this way, except by maintaining quite a high degree of heat near the balance, which was not attempted. These were taken with an ordinary specific gravity flask with a perforated stopper, which was filled with the melted fat at convenient temperatures, then allowed to cool, and weighed. In this way I took the specific gravities of the more important samples used in the investigations, not only the harder fats, such as stearines, but also the lards and oils. Being interested in examining for myself the correctness of the figures given by Allen for the expansions of these bodies, I determined the specific gravities upon all the samples at high temperatures, and from these data the coefficients of expansion in each case. As these samples were typical in many cases, and as all were subjected to a very thorough and careful examination in respect of their other properties (the results of which will be set forth in the Bulletin), I append a table containing the results obtained, as they may prove valuable in establishing standards for this important class of food materials, the composition of which is attracting much attention at present among chemists.

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[1] Organic Analysis 2, 14, foot-note.

All the determinations were made very carefully, and the figures given are in all cases the average of two or more duplicates. In the densities taken at low temperatures, the flasks filled with the sample were placed in a vessel containing water somewhat above the temperature at which the determination was to be made, and when it had dropped to this point they were carefully stoppered, taken out of the vessel, allowed to cool, and weighed. The determinations at high temperatures were made by placing the flasks in an oil-bath. The heat was raised to as high a point as was deemed safe, and at the temperatures used, 190°–200° C., there was scarcely a darkening of the contents of the flasks, and I am convinced that no decomposition had taken place which would alter appreciably the density of the sample. From the densities taken at these two widely different temperatures, the mean increase in density and the mean coefficient of expansion were determined for each sample. The formula used for this was the one usually given in the books,[1] $\delta = \frac{D_0' - D_0}{(t' - t)D_0}$, in which

$D_0 =$ density at the lower observed temperature;
$D_0 =$ " " higher " "
$t =$ lower temperature;
$t' =$ higher "

although it appears to me that the formula $\frac{D_0 - D_0'}{(t' - t)D_0}$ would be more correct, or $\frac{D_0 - D_0'}{(t' - t)\left(\frac{D_0 + D_0''}{2}\right)}$ still better. Great confusion exists in chemical literature in the expression of specific gravities. I have referred all my results to water at $+4°$ C., believing that eventually all specific gravities will be stated in these terms, as is the custom in continental Europe. The absolute densities are calculated from the formula $\Delta = \delta + \kappa$, in which

$\Delta =$ coefficient of absolute expansion in glass;
$\delta =$ " " apparent " "
$\kappa =$ " " cubical expansion of glass $= .000025$.

The weights were not reduced to a vacuum, and no correction was made for the thread of mercury projecting above the bulb.

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[1] Watts' Dictionary 3, 71.

Specific Gravities of Fats and Oils at Various Temperatures, with Mean Coefficients of Expansion.

DESCRIPTION.	Temperature.	Apparent Specific Gravity in Glass Vessels.	Absolute Specific Gravity.	Temperature.	Apparent Specific Gravity in Glass Vessels.	Absolute Specific Gravity.	Range in Temperature.	Mean Difference in Specific Gravity for each Degree Centigrade Apparent in Glass Vessels.	Mean Coefficient of Expansion Apparent in Glass Vessels.	Mean Coefficient of Expansion, Absolute.	Calculated.			
											Specific Gravity $d = \frac{+15.5^\circ}{+4^\circ}$ C. Apparent.	Specific Gravity $d = \frac{+40^\circ}{+4^\circ}$ C. Apparent.	Specific Gravity $d = \frac{+50^\circ}{+4^\circ}$ C. Apparent.	Specific Gravity $d = \frac{+100^\circ}{+4^\circ}$ C. Apparent.
Lards.														
Leaf Lard rendered in Laboratory U. S. Dept. Agriculture............	$\frac{+40^\circ}{+4^\circ}$ C.	.89679	.89769	$\frac{+190^\circ}{+4^\circ}$ C.	.80475	.80940	$+40^\circ$ to $+190^\circ$ C.	.0006136	.0007624	.0007649	.91181	.89679	.89065	.85997
Intestinal Lard rendered in Laboratory U. S. Dept. Agriculture.......	"	.89635	.89725	"	.80315	.80780	"	.0006213	.0007736	.0007761	.91157	.89635	.89014	.85907
Head Lard rendered in Laboratory U. S. Dept. Agriculture..........	"	.89816	.89906	"	.80512	.80977	"	.0006203	.0007704	.0007729	.91336	.89816	.89195	.86094
Squire's Pure Lard, made by J. P. Squire & Co., Boston, Mass...	"	.89700	.89790	$\frac{+95^\circ}{+4^\circ}$	.86319	.86546	$+40^\circ$ to $+95^\circ$	.0006147	.0007122	.0007147	.91206	.89700	.89085	.86012
Cassard's Pure Lard, made by Cassard & Co., Baltimore, Md..........	"	.89848	.89938	$\frac{+187^\circ}{+4^\circ}$	.80888	.81345	$+40^\circ$ to $+187^\circ$	.0006095	.0007535	.0007560	.91341	.89238	.89848	.86191
[1]Armour's "Compound Lard," made by Armour & Co., Chicago, Ill..	"	.89940	.90030	$\frac{+190^\circ}{+4^\circ}$	.80646	.81111	$+40^\circ$ to $+190^\circ$	.0006196	.0007683	.0007708	.91458	.89940	.89320	.86222
Armour's "Compound Lard," made by Armour & Co., Chicago, Ill...	"	.89854	.89944	"	.80522	.80987	"	.0006221	.0007726	.0007751	.91378	.89232	.89854	.86121
Fairbanks' "Compound Lard," made by Fairbanks & Co., Chicago, Ill.	"	.90000	.90090	"	.80724	.81189	"	.0006184	.0007660	.0007685	.91515	.90000	.89382	.86289
Lard Stearines.														
Lard Stearine used in compounding Armour's Compound Lard........	$\frac{+50^\circ}{+4^\circ}$	.88836	.88951	$\frac{+200^\circ}{+4^\circ}$	.79579	.80069	$+50^\circ$ to $+200^\circ$	.0006171	.0007755	.0007780	.90965	.89453	.88836	.85750
Lard Stearine used in compounding Fairbanks' Compound Lard.......	"	.88850	.88965	"	.79677	.80167	"	.0006115	.0007675	.0007700	.90959	.89461	.88850	.85792
Beef Fat and Oleostearines.														
Pure Beef Fat from the testicle, obtained from Prof. S. P. Sharpless...	$\frac{+50^\circ}{+4^\circ}$	.88998	.89113	$\frac{+190^\circ}{+4^\circ}$	.80289	.80754	$+50^\circ$ to $+190^\circ$	.0006221	.0007748	.0007773	.91144	.89620	.88998	.85888
Oleostearine used in compounding Armour's Compound Lard..........	"	.88615	.88730	$\frac{+200^\circ}{+4^\circ}$	.79487	.79977	$+50^\circ$ to $+200^\circ$	.0006085	.0007656	.0007681	.90714	.89223	.88615	.85572
Oleostearine used in compounding Fairbanks' Compound Lard........	"	.88523	.88638	"	.79286	.79776	"	.0006158	.0007767	.0007792	.90647	.89138	.88523	.85444
Cottonseed Stearine obtained from Prof. D. Wesson................	$\frac{+40^\circ}{+4^\circ}$	.90313	.90403	$\frac{+190^\circ}{+4^\circ}$	.80689	.81154	$+40^\circ$ to $+190^\circ$	.0006416	.0007951	.0007976	.91884	.90313	.89671	.86463
Cottonseed Oils.														
Crude Cottonseed Oil obtained from Prof. D. Wesson............. ...	$\frac{+23^\circ}{+4^\circ}$	.91548	.91595	$\frac{+190^\circ}{+4^\circ}$	.81118	.81583	$+23^\circ$ to $+190^\circ$	.0006245	.0007699	.0007724	.92016	.90486	.89862	.86739
Crude Cottonseed Oil obtained from Southern Cotton Oil Trust.	"	.91744	.91791	"	.81573	.82038	"	.0006090	.0007466	.0007491	.92200	.90708	.90099	.87054
[2]"Summer Yellow" Oil obtained from Southern Cotton Oil Trust.....	"	.91589	.91636	"	.81021	.81486	"	.0006328	.0007813	.0007838	.92063	.90514	.89880	.86716
"Summer White" Oil obtained from Southern Cotton Oil Trust......	"	.91578	.91625	"	.80959	.81424	"	.0006359	.0007858	.0007883	.92055	.90497	.89861	.86681
"Winter Yellow" Oil obtained from Southern Cotton Oil Trust......	$\frac{+24^\circ}{+4^\circ}$	.91623	.91673	"	.80525	.80990	$+24^\circ$ to $+190^\circ$	.0006685	.0008302	.0008327	.92191	.90553	.89885	.86542
"Winter White" Oil obtained from Southern Cotton Oil Trust........	"	.91636	.91686	"	.81017	.81482	"	.0006397	.0007896	.0007921	.92179	.90612	.89972	.86774
Refined Cottonseed Oil used in compounding Armour's Compound Lard	$\frac{+23^\circ}{+4^\circ}$	.91667	.91714	"	.80925	.81390	$+23^\circ$ to $+190^\circ$	.0006432	.0007948	.0007973	.92150	.90573	.89930	.86714
Olive Oils.														
Pure Olive Oil obtained from Z. D. Gilman, Washington, D. C........	$\frac{+23^\circ}{+4^\circ}$	.91079	.91126	$\frac{+190^\circ}{+4^\circ}$	.80430	.80885	$+23^\circ$ to $+190^\circ$	.0006377	.0007928	.0007953	.91557	.89995	.89351	.86168
Pure Olive Oil obtained from Prof. S. P. Sharpless....................	"	.91034	.91081	"	.80538	.81003	"	.0006285	.0007804	.0007829	.91505	.89965	.89337	.86194

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[1] Armour's Compound Lards are made by the following formulæ, according to affidavits filed with the samples:

	Regular (No. 7 of above table).	"Export" (No. 6 of table).
Lard	67 per cent.	59 per cent.
Oleostearine...............	15 "	18 "
Refined Cottonseed Oil..	18 "	23 "
	100	100

[2] Trade terms used to designate different grades of refined oils.

The specific gravities of the different samples at various temperatures are also given in the last columns of the table, these having been calculated by means of the coefficients of expansion.

It will be seen that the results confirm, in the main, Allen's[1] conclusions in regard to the generally uniform rate of expansion of all fats and oils. The average increase in density in my samples would be rather lower than the figure he gives (.00064) for each degree C., as his figure was calculated from the formula $\delta = \frac{D_0 - D_0'}{(t'-t)D_0}$. Kopp[2] gives a figure slightly higher than mine for the mean absolute expansion-coefficient of olive oil, viz. .00080348.

In the lards and oils in the above table I also determined the density by the plummet at + 35° C. These results, together with the results calculated from the flask determinations, so as to make the figures comparable, are given in the following table:

Comparison of Results with Plummet and with Specific Gravity Flask.

Lards.	With Plummet. $d = \frac{+35^\circ}{+35^\circ}$ C.	With Specific Gravity Flask. $d = \frac{+35^\circ}{+35^\circ}$ C.
1	.9058	.90508
2	.9047	.90484
3	.9066	.90652
4	.9044	.90523
5	.9067	.90671
6	.9069	.90797
7	.9068	.90667
8	.9080	.90816
Cotton Seed Oils.		
1	.9151	.91391
2	.9164	.91510
3	.9134	.91377
4	.9132	.91357
5	.9154	.91412
6	.9138	.91475
7	.9133	.91452
Olive Oils.		
1	.9076	.90848
2	.9080	.90811
Mean,	.9098	.90985

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[1] Op. cit. p. 20.

[2] Ann. Chem. (Liebig) 93, 129.

This short series of comparisons adds testimony to the accuracy of the Archimedian method for taking specific gravities. It is certainly a most rapid and convenient method for fats and oils. I went through nearly the entire series of samples used in our lard investigation, about 150 in all, in three days. I would call attention to a slight inaccuracy in Allen's description of the method. On page 14 (Vol. II), he says, "The plummet should have a displacement of exactly 5 *cubic centimeters*" (in water). This should, of course, be 5 *grams*, otherwise he would be comparing *volume* with *weight*, as it is the *weight* of the sample displaced which is used as the numerator of the fraction of which the *weight* of water displaced is the denominator in the expression of its specific gravity. The error would not be so great where the volume and density of water were taken as being identical at 15.5° C., but still quite an appreciable error would be introduced when the determination on the sample was made at 35°–50° C., as on a fat for example. There is much need for more exact mathematics in calculating specific gravities, and more uniformity in methods of expressing them among chemists is greatly to be desired.

Contributions from the Sheffield Laboratory of Yale University.

XXXI.—ON NITRO-DERIVATIVES OF OXALTOLUIDE.

By W. G. Mixter and F. Kleeberg.

Ortho-oxaltoluide.—Ladenburg,[1] by heating equal parts of *o*-toluidine and anhydrous oxalic acid, obtained polyformtoluide, melting point 211°. When, however, *o*-toluidine is heated with half its weight of crystallised oxalic acid to 190°, *o*-oxaltoluide is formed, and apparently no polyformtoluide. That is, with an excess of oxalic acid polyformtoluide results, and with an excess of toluidine oxaltoluide. We heated a mixture of oxalic acid and *o*-toluidine cautiously in a flask so that but little toluidine escaped with the vapor of water, and when the temperature of the molten mass had risen to 190°, it was poured into dilute hydrochloric acid. The lumps were broken up and the product was thoroughly washed with water. It was further purified by solution in boiling alcohol, from which it crystallised on cooling. An analysis of the preparation gave results which corresponded closely with the composition of oxaltoluide; but since this compound differs empirically from formtoluide by one atom of hydrogen, the analysis does not prove its purity. Moreover, our preparation melted at 199°–201°, or above the melting point, 189°, given by Mauthner and Suider[1] for *o*-oxaltoluide, which was first obtained by them by heating together ethyl oxalate and *o*-toluidine. The ready solution of our preparation of *o*-oxaltoluide in hot alcohol indicated that it was, at least, not largely mixed with polyformtoluide, which is only slightly soluble in the same solvent. Further, we prepared *o*-oxaltoluide as described by Mauthner and Suider, and found it to have the same melting point as that from heating oxalic acid and toluidine, and also found the preparations by the two methods to have identical properties. The yield of *o*-oxaltoluide is considerably larger with oxalic acid than when ethyl oxalate is used.

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[1] Ber. d. chem. Ges. **10**, 1128.

Tetra-nitro-o-oxaltoluide. — *o*-Oxaltoluide, 19.7 grams, was added slowly to 210 cc. of fuming nitric acid, and the clear red solution obtained was heated on a water-bath to boiling and then poured into cold water. The yellow product which separated was washed thoroughly with water and dried at 100°. The yield was 25 grams. The following analyses were made by Mr. F. O. Walther, who commenced the investigation in this laboratory, but did not have time to complete the work before leaving:

I. 0.5243 gram gave 82.87 cc. N at 16.7° and 769.1 mm. 0.4091 gram gave 0.1058 gram H_2O and 0.6415 gram CO_2.

II. 0.2596 gram gave 41.62 cc. N at 16.5° and 764.4 mm. 0.3981 gram gave 0.1098 gram H_2O and 0.6266 gram CO_2.

	Theory.	I.	II.
C_{16}	42.86	42.76	42.92
H_{12}	2.68	2.87	3.08
N_6	18.75	18.93	19.10
O_{10}	35.71	...	...

In order to determine the constitution of this tetranitro-oxaltoluide, the following experiments were made: First, 12 grams of it were digested with a boiling solution of potassium hydroxide (density 1.27) until ammonia ceased to come off. On adding hydrochloric acid, carbon dioxide was copiously evolved, and a black substance separated which was washed, dissolved in ether, filtered, and the solution evaporated. The tarry residue remaining appeared to be a mixture. Another portion of tetranitro-oxaltoluide was digested with a very dilute solution of potassium hydroxide, in which it dissolved completely. Hydrochloric acid was then added to the solution, and the yellow precipitate obtained was analysed and found to be tetranitro-oxaltoluide. Next, tetranitro-oxaltoluide was dissolved in concentrated sulphuric acid, the temperature of the mixture being gradually raised to 150°. The solution, after cooling, was poured into water, and the yellow precipitate which formed was washed, and, after recrystallising from hot alcohol, melted at 208°, the melting point of dinitro-*o*-toluidine, $C_6H_2CH_3\overset{2}{N}H_2\overset{3}{N}O_2\overset{5}{N}O_2$, described by Staedel.[1] In order to prove conclusively the constitution of the dinitro-toluidine in hand, it was converted into dinitro-toluene, as follows: It was added to concentrated nitric acid, and nitrous fumes passed through the mixture, which was kept cool, and was finally poured into boiling absolute alcohol. The product, after recrystallising, melted at 90°, thus proving its identity with the symmetrical dinitro-toluene described by Staedel, having the constitution $C_6H_3\overset{1}{C}H_3\overset{3}{N}O_2\overset{5}{N}O_2$. From these results it follows that tetranitro-*o*-oxaltoluide has the constitution

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[1] Monatsh. der Chemie 7, 233.

$$\begin{array}{l}CO\overset{1}{C}H_3\overset{2}{N}HC_6H_2\overset{3}{N}O_2\overset{5}{N}O_2\\ |\\ CO\underset{1}{C}H_3\underset{2}{N}HC_6H_2\underset{3}{N}O_2\underset{5}{N}O_5.\end{array}$$

It is white, slightly soluble in hot absolute alcohol and glacial acetic acid, insoluble in ether and benzene, but dissolves readily in warm nitrobenzene, from which it crystallises on addition of absolute alcohol. It decomposes without showing a sharp melting point at about 270°.

An attempt was made to obtain a hexnitro-derivative by adding 10 grams of *o*-oxaltoluide to 100 cc. of red fuming nitric acid, and after complete solution adding 100 cc. of concentrated sulphuric acid. The whole was heated over a lamp to boiling, then allowed to cool and poured into snow. The product after drying weighed 11.5 grams. Two determinations gave 19.43 and 19.32 per cent.; calculated for hexnitro-oxaltoluide 20.82 per cent. These results indicate an impure tetranitro-oxaltoluide.

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[1] Ber. d. chem. Ges. **14**, 900.

The *p*-oxaltoluide used in the following experiments was made according to the method described by Hübner,[1] by heating together equal parts of *p*-toluidine and oxalic acid. The product was treated with boiling water and finally with boiling alcohol.

Dinitro-p-oxaltoluide.—This compound was obtained by Hübner[2] by adding *p*-toluidine to red fuming nitric acid. We have prepared the same substance by using 15 parts of nitric acid of density 1.4 and boiling for five minutes.

Tetranitro-p-oxaltoluide.—This compound is formed when *p*-oxaltoluide is nitrated by hot red fuming nitric acid, or by a mixture of this acid and concentrated sulphuric acid, as shown by the following results: *p*-oxaltoluide, 5 grams, was added gradually to 50 cc. of fuming nitric acid, in which it dissolved completely. The solution on heating on a water-bath for a few minutes deposited crystals. The mixture was then poured into cold water, when a further separation occurred. The product after washing and drying at 100° weighed 5.7 grams. It is designated as A.

Another portion of 5 grams of *p*-oxaltoluide was added to a mixture of 50 cc. of fuming nitric acid and 50 cc. of sulphuric acid. The reaction was very violent and the yield was 5 grams. This product is designated as B.

A third portion of 5 grams of *p*-oxaltoluide was added to 100 cc. of fuming nitric acid, and then 100 cc. of concentrated sulphuric acid were poured in. Yellow crystals separated on shaking. The mixture was heated on a water-bath for ten minutes, then poured into cold water, filtered, washed free from acid, and dried at 100°. The product, designated as C, weighed 4.7 grams.

Analysis of A.—0.3106 gram gave 0.4817 gram CO_2 and 0.0762 gram H_2O. 0.457 gram gave 71.17 cc. N at 7.3° and 755 mm.

Analysis of B.—0.4520 gram gave 69.6 cc. N at 7.2° and 760.2 mm.

Analysis of C.—0.3738 gram gave 0.5801 gram CO_2 and 0.0935 gram H_2O. 0.4187 gram gave 63.82 cc. N at 5.6° and 767.4 mm.

	Theory.	A.	B.	C.
C_{16}	42.86	42.29	...	42.32
H_{12}	2.68	2.72	...	2.77
N_6	18.75	18.93	18.85	18.94
O_{10}	35.71	...	...	...
	100.			

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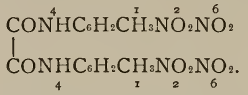
[1] Ann. Chem. (Liebig) **209**, 371.

[2] Ber. d. chem. Ges. **8**, 474.

The tetranitro-*p*-oxaltoluide yielded, when saponified by a hot dilute solution of potassium hydroxide, a dinitrotoluidine melting at 168° and easily soluble in alcohol, corresponding to the one described by Beilstein[1] with the constitution $C_6H_2\overset{1}{C}H_3\overset{2}{N}O_2\overset{4}{N}H_2\overset{6}{N}O_2$. The tetranitro-*p*-oxaltoluide has therefore the constitution



$$\begin{array}{l} CO\overset{4}{N}HC_6H_2\overset{1}{C}H_3\overset{2}{N}O_2\overset{6}{N}O_2 \\ | \\ CO\underset{4}{N}HC_6H_2\underset{1}{C}H_3\underset{2}{N}O_2\underset{6}{N}O_2. \end{array}$$

It is insoluble in the ordinary solvents, but readily soluble in warm nitrobenzene. Both it and the corresponding ortho-compound do not yield with potassium hydroxide a dinitrotolyloxamide. In conclusion it may be stated that the tetranitro-derivatives of ortho- and para-oxaltoluide are easily made, and hence are good compounds from which to prepare dinitrotoluidines. We have not obtained satisfactory results in attempting to nitrate oxalxylidine.

A METHOD FOR THE DETECTION OF CHLORINE, BROMINE, IODINE, AND SULPHUR IN ORGANIC COMPOUNDS.

By Charles W. Marsh.

In testing for sulphur according to Schönn[2] by heating an organic substance with metallic sodium in a closed tube, dissolving the sodium sulphide formed in water, and adding a solution of sodium nitro-prusside, the inconvenience of working with sodium, and the precautions necessary in heating the sodium and substance, and in adding water to the contents of the tube, led the writer to look for another metal to replace the sodium. This metal when heated with organic bodies should decompose them and combine with the halogens and sulphur, or, if the substance were decomposed by heat, would enter into like combination.

Magnesium in fine powder has also been recommended by Schönn,[3] but only for the estimation of sulphur. He heats the substance with powdered magnesium in a hard glass tube, allows it to cool, adds a little water and heats. The liquid is filtered and a solution of sodium nitro-prusside added, and this reacts for sulphur by giving a reddish-violet coloration.

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[1] Ber. d. chem. Ges. **13**, 243.

[2] Ztschr. anal. Chem. 8, 52.

[3] Ibid 8, 398.

Powdered zinc having the property of decomposing organic substances when heated with them, it seemed that this might be a ready substance to decompose organic bodies, and at the same time to unite with the halogens to form chloride, bromide or iodide, as the case might be, all of which are soluble in water. From the water solution the corresponding silver salt would be precipitated, which would aid to identify the halogen in the substance treated.

The substances containing sulphur in any form of combination would on heating with zinc form zinc sulphide. This could be decomposed by the addition of hydrochloric acid direct to the tube containing the zinc and charred residue of the organic substance, if any, and the sulphuretted hydrogen gas then tested for at the mouth of the tube by means of a narrow strip of filter-paper moistened with lead acetate solution.

The method of procedure outlined was tried on many organic substances containing chlorine, bromine, iodine, and sulphur, and gave the expected results. Several organic substances containing no chlorine, bromine or iodine were treated in the same manner, and a white precipitate invariably appeared on the addition of nitric acid and silver nitrate solution. The distilled water was tested, but gave no reaction for chlorine. A small quantity of zinc was shaken with water, the liquid poured on a filter, and to the filtrate nitric acid and silver nitrate solution were added, and immediately a white precipitate appeared, which was soluble in ammonium hydrate and reprecipitated by nitric acid, showing the presence of a large quantity of chlorine in the zinc. The test for sulphur was made as described, a brown color being obtained on the lead acetate paper, showing the presence of a small amount of sulphur. The zinc was some used in the organic laboratory work, and came in the form of powder. As the zinc used contained chlorine and sulphur, the tests already made were valueless.

Another sample of fine zinc used in the reduction of ferric iron solutions was treated for chlorine and gave no reaction. It also gave no reaction for sulphur. This zinc comes in a spherical form, the diameters of which are mostly half a millimeter. The experiments made with the impure zinc were repeated with the pure sample, and also on several other compounds. The test on substances containing no chlorine, bromine, iodine nor sulphur were made, and in no case was a distinct reaction obtained. In but one case an opalescence appeared after the addition of nitric acid and silver nitrate solution, while in all the others the solution remained perfectly clear. No trace of sulphur could be detected. This proved that the decomposition of organic substances on heating would not give reactions similar to the ones characteristic of the elements sought.

The substance was heated in about the same manner in every case, with a few exceptions, which will be described. Many of the tests were made in small hard-glass closed tubes, such as are used in blowpipe analysis, having an internal diameter of five millimeters and a length of sixty millimeters. Four-inch test tubes were found to give as satisfactory results.

The exact details of manipulation are as follows:

The substance is first introduced into the tube and then the zinc is added in about equal volume. They are intimately mixed by shaking. The tube is held in a slanting position, with the lower end in the flame, and heated slowly. In many cases the substance volatilises, condenses in the upper end of the tube, and runs down upon the hot zinc, when it is decomposed. In others it carbonises and a watery colored liquid distills.

If combustible gases or vapors are given off, they are lighted. It is better not to heat the tube red hot, for in that case the zinc would melt to a globule and inclose some of the zinc salt formed. At the same time the zinc chloride, bromide and iodide would be volatilised and thus cause a loss. Zinc sulphide is not volatile.

If a liquid is under examination, it is better to use a test-tube, as the mouth is wider. The liquid is first added to the test-tube, which moistens the sides, so that when the zinc is added it will adhere to the inner walls and some remain near the mouth. The test-tube, held in a wooden holder, is slightly heated, and the vapors, if inflammable, are ignited, while the tube is held in a position nearly horizontal. The heat is so regulated that the flame will be as small as possible, and will tend to burn down in the tube and there act upon the zinc adhering to the sides. With the liquids methyl iodide, ethyl iodide and carbon disulphide, this was the only method by which reactions for iodine and sulphur could be obtained. With para-dichlor-benzene this last method gave good results, whereas the general method of heating gave no reaction for chlorine.

After heating with zinc, the residue in the tube is cooled and treated as follows:

For Chlorine.—About one cubic centimeter of distilled water is added direct to the test-tube, the whole shaken and allowed to stand, while a small filter is fitted to a funnel. The liquid is now poured on the filter and caught in a short test-tube placed underneath. The filtrate is acidified with nitric acid and a solution of silver nitrate added. A white precipitate of silver chloride, soluble in ammonium hydrate and reprecipitated by nitric acid, was obtained from the following substances tested:

Liquids.—Chloroform, acetyl chloride, ethylene chloride, allyl chloride.

Solids.—Mono-chlor-crotonic acid, para-di-chlor-benzene, tri-chlor-phenol.

For Bromine.—The contents of the tube are treated with water and filtered, as in the test for chlorine. The filtrate is divided into two parts. In one part nitric acid and silver nitrate solution are added, when the light yellow precipitate of silver bromide appears. To the other part of the filtrate nitric acid is added and a few drops of carbon disulphide. The carbon disulphide is colored brown from the bromine liberated. In several cases the precipitate of silver bromide was very slight, but in every case the carbon disulphide was strongly colored.

The following substances gave the reactions described:

Liquids.—Acetyl bromide, amyl bromide, iso-butyl bromide, brom-toluene.

Solids.—Tribrom-aniline, ortho-nitro-dibrom-phenyl-propionic acid, dibrom-benzene, mono-brom-camphor, di-brom-camphor, eosine, di-brom-gallein, dibrom-anthraquinone, di-brom-anthracene.

For Iodine.—The filtrate is divided and treated as in the case of bromine. Yellow silver iodide is obtained in the first instance, and the carbon disulphide colored violet by the iodine freed from the zinc by the nitric acid in the second.

Iodine was thus detected in the following substances:

Liquids.—[1] Methyl iodide, ethyl iodide, allyl iodide, iso-butyl iodide.

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[1] The liquid iodides used were more or less decomposed and colored by iodine set free. In order to work upon undecomposed chemicals, they were each separately shaken with potassium hydrate solution, to take up the iodine, and the resulting colorless alcoholic iodide was repeatedly washed with water. The iodides thus treated were used for the experiments.

Solids.—Iodoform.

For Sulphur.—To the tube containing the residue after heating the substance with zinc, a few drops of hydrochloric acid are added, and the hydrogen sulphide generated identified as it escapes from the mouth of the tube by filter-paper moistened with lead acetate solution. The paper is turned brown almost immediately. There is no necessity for heating the tube. The compounds in the list gave distinct reactions.

Liquids.—Carbon disulphide, allyl mustard oil, ethyl sulphocyanate.

Solids.—Sulpho-urea, potassium amyl sulphate, sulphanilic acid, ammonium di-phenyl-amid-azo-benzene sulphonate, saccharin, sodium beta-naphthol di-sulphonate, mono-sodium anthraquinone sulphonate, morphine sulphate.

It is claimed that, by using the process described, chlorine, bromine, iodine, and sulphur can be accurately and rapidly detected in organic compounds by the use of apparatus and chemicals ordinarily found in chemical laboratories.

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SPECIFIC VOLUME OF CAMPHOR AND OF BORNEOL DETERMINED WITH PROXIMATE ACCURACY.

BY MITSURU KUHARA.

The materials employed in the experiments were ordinary commercial camphor and borneol, purified by repeated sublimation. Their melting and boiling points[1] were found to be as follows:

	Melting point.	Boiling point.
Camphor,	177.7°	205.3°
Borneol,	...	209.7

In these determinations a number of experiments were repeated, and in each the necessary corrections were made.

The determination of the specific gravity of liquid camphor and of liquid borneol was made with the use of a cylindrical specific gravity bottle of small size, whose capacity had carefully been ascertained by filling it with boiled distilled water. Either the camphor or the borneol was fused in a long cylindrical vessel over the paraffin bath, and the specific gravity bottle and its stopper, tied separately with platinum wire, were both introduced into this cylindrical vessel and heated together with the melted camphor or borneol. As the boiling point of the liquid camphor and of the liquid borneol is always found a few degrees higher than that of the vapor, the moment the temperature of the liquid reached 205.3° or 209.7° (boiling points of their vapors), the stopper was instantly closed and the bottle filled with the liquid was taken out, cooled and weighed. These experiments were conducted under a higher barometric pressure than the normal, all the measurements being made by means of the corrected thermometer. The specific gravity was calculated according to the following formula, referring to the water of 4°:

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[1] In most text-books the melting and boiling points of camphor are given to be 174° and 204° respectively, and the boiling point of borneol to be 212°.

$$\text{Specific gravity} = \frac{W}{V(1 + 3\beta)(T - t)}.$$

W = Weight of the liquid camphor or borneol at T.
T = Boiling point of camphor or borneol.
V = Volume of water at t (or the capacity of the bottle at t).
t = Temperature when the bottle filled with water was weighed.
3β = Coefficient of the cubical expansion of glass = 0.0000254.

I.—*Experiments on Camphor*, $C_{10}H_{16}O$.

The following three experiments were performed with a bottle of the capacity of 6.28114 cc. at 30.5°.

(1) Camphor in the bottle weighed 5.1304 grams at 205.3°.
(2) " " " 5.1089 " "
(3) " " " 5.1189 " "

The fourth experiment was performed with a bottle of the capacity of 2.98632 cc. at 40.5°.

(4) Camphor in the bottle weighed 2.4252 grams at 205.3°.

Seven more experiments were performed with a bottle of the capacity of 2.74518 cc. at 40.5°.

(5) Camphor in the bottle weighed 2.2400 grams at 205.3°.
(6) " " " 2.2470 " "
(7) " " " 2.2405 " "
(8) " " " 2.2330 " "
(9) " " " 2.2355 " "
(10) " " " 2 2290 " "
(11) " " " 2.2315 " "

Specific gravity at 205.3° deduced according to the formula given above:

(1) 0.8131
(2) 0.8097
(3) 0.8113
(4) 0.8087
(5) 0.8125
(6) 0.8147
(7) 0.8127
(8) 0.8100
(9) 0.8109
(10) 0.8085
(11) 0.8094

Mean, 0.8110.

$$\text{Specific volume}=\frac{\text{molec. wt.}}{\text{sp. gravity}}=\frac{152}{0.811}=187.42$$

II.—*Experiments on Borneol,* $C_{10}H_{18}O$.

The experiments were performed with a bottle of the capacity of 2.74518 cc. at 40.5°.

(1) Borneol in the bottle weighed 2.2284 grams at 209.7°.
(2) " " " 2.2284 " "
(3) " " " 2.2265 " "
(4) " " " 2.2245 " "
(5) " " " 2.2390 " "
(6) " " " 2.2258 " "

Specific gravity at 209.7°.

(1) 0.8082
(2) 0.8082
(3) 0.8075
(4) 0.8071
(5) 0.8120
(6) 0.8073

Mean, 0.8083.

$$\text{Specific volume}=\frac{\text{molec. wt.}}{\text{sp. gravity}}=\frac{154}{0.8083}=190.5$$

The specific volume of camphor and that of borneol calculated with Kopp's values of the atomic volumes of carbon, hydrogen, and oxygen, regarding the former as a ketone and the latter as an alcohol, are found to be as follows:

	Camphor.			Borneol.	
C_{10}	10 × 11 =	110	C_{10}	10 × 11 =	110
H_{16}	16 × 5.5 =	88	H_{18}	18 × 5.5 =	99
O	1 × 12.2 =	12.2	O	1 × 7.8 =	7.8
Specific volume,		210.2			216.8

Thus it is seen that the calculated values are much greater than those found by experiment. Also the specific volume of benzene and of some of its derivatives, calculated with Kopp's values, is often found to be much greater than those obtained experimentally. In Watts' Dictionary of Chemistry, 3d Supplement, page 2126, the following statements are given: "Lothar Meyer makes $H = 3$, and Löschmidt $C = 14$ and $H = 3.5$; and by assuming that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value 3.5, we obtain a value for this hydrocarbon which is identical with the observed values." Thus:

Calculated.

$$\left.\begin{array}{ll} C_3 & 3 \times 14 = 42 \\ C_3 & 3 \times 11 = 33 \\ H_6 & 6 \times 3.5 = 21 \end{array}\right\} 96$$

Found.	
Kopp.	Ramsay.
95.8	95.9

I tried to apply these values of carbon and hydrogen and Kopp's values of oxygen (12.2 and 7.8) to camphor and borneol, supposing each to consist of a closed chain of six carbon atoms like benzene, and I found that the calculated specific volumes are almost concordant with those observed.

Camphor.

$$\left.\begin{array}{l} C_3 = 3 \times 14 \\ C_7 = 7 \times 11 \\ H_{16} = 16 \times 3.5 \\ O = 1 \times 12.2 \end{array}\right\} \begin{array}{cc} \text{Calculated.} & \text{Found.} \\ 187.2 & 187.42 \end{array}$$

Borneol.

$$\left.\begin{array}{l} C_3 = 3 \times 14 \\ C_7 = 7 \times 11 \\ H_{18} = 18 \times 3.5 \\ O = 1 \times 7.8 \end{array}\right\} \begin{array}{cc} \text{Calculated.} & \text{Found.} \\ 189.8 & 190.5 \end{array}$$

I tried further to compute the specific volumes of some of the benzene derivatives whose experimental numbers are already known by applying a similar method of calculation to them, thus:

	Found.			Calculated.	
	Kopp.	Ramsay.	Yoshida.	$C = 14$ & 11; $H = 3.5$; $O = 12.2$ & 7.8.	$C = 11$; $H = 5.5$; $O = 12.2$ & 7.8.
Benzene,	95.8	95.9	...	86.0	99.0
Phenol,	103.6	106.9	...	103.8	106.9
Benzyl alcohol,	123.7	...	...	121.8	128.8
Benzaldehyde,	118.4	...	...	119.2	122.2
Ethyl benzoate,	172.4–174.8	...	163.1[1]	162.0	174.0
Benzoic acid,	126.9	...	...	127.0	130.0
Naphthalene,	149.2	...	...	150.0	154.0

It thus appears that the numbers found by the new way of calculation agree better with the observed ones in some cases than with those calculated with Kopp's values.

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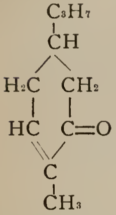
[1] This number was observed according to Ramsay's method by Mr. H. Yoshida, Science College, Imperial University of Tokio.

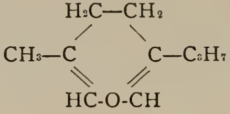
Now, the principal formulæ for camphor suggested by different chemists are six in number, namely:

(1)



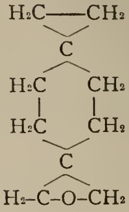
Kekulé.

(2)



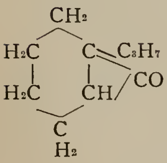
Victor Meyer.

(3)



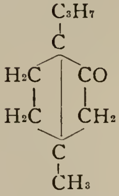
Hlasiwetz.

(4)



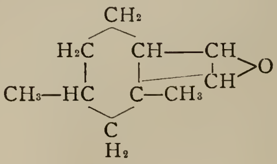
Kachler.

(5)



Kanonnikow.

(6)



Armstrong.

If we suppose the above method of calculation to be true, there may exist in camphor a closed chain of six carbon atoms, and camphor itself may be a ketone, and then the formula 1, 4 or 5 may represent its constitution, as any one of the remaining formulæ would represent it as an oxide. Kanonnikow,[1] however, who determined the refraction equivalent of camphor and of its allied compounds by applying Brühl's method, states that camphor has no double union between carbon atoms. Hence, it may be concluded that one of the formulæ 4 and 5 represents the constitution of camphor, and borneol is its corresponding alcohol.

Chemical Laboratory, First Kōto-chiu-Gakko, Tokio, Japan, *July*, 1883.

(1) Ber. d. chem. Ges. **6**, 929.
(2) Ibid. **3**, 116.
(3) Ibid. **3**, 540.
(4) Ann. Chem. (Liebig) **165**, 185.
(5) Ber. d. chem. Ges. **16**, 3051.
(6) Ibid. **11**, 1698.

[1] Ber. d. chem. Ges. **16**, 3051.

A RAPID COLORIMETRIC METHOD OF DETERMINING NITRATES IN POTABLE WATERS.[1]

By Samuel C. Hooker.

[Read at the Stated Meeting of the Chemical Section of the Franklin Institute, March 19, 1889.]

In devising a process for the estimation of nitrates in the minute quantities in which they occur in natural waters, I have not been ignorant of the fact that there are already several very satisfactory ways in which this can be accurately done. I have, however, aimed at greater rapidity than has heretofore been possible.

Fully fifteen years ago, Graebe and Glaser discovered carbazol, and observed that when dissolved in concentrated sulphuric acid, it gave rise to an intensely green solution on the addition of nitric acid. This reaction, which up to the present time has been used only as a means of identifying carbazol, forms the basis of the process to be described. Its extraordinary delicacy renders it particularly suitable for the purposes of water analysis, and enables a quantity of nitric acid, containing as little as $\frac{6}{10000}$ of a milligram of nitrogen, to be accurately determined. The reaction is not, however, peculiar to nitric acid; all oxidising agents behave similarly. Graebe and Glaser enumerate chlorine, bromine, iodine, nitrous and chromic acids as giving rise to the same intensely colored solution. With the exception of nitrous acid, the substances just mentioned are almost invariably absent from natural waters, and may therefore be dismissed from further consideration. There is, however, one other oxidising agent, namely iron in the ferric condition, which is sometimes found in very appreciable quantities, and it therefore became necessary, in studying the influence of the substances in solution upon the process, to give special attention to iron as well as to nitrous acid.

As the result of a number of careful experiments, the following conclusions were arrived at with regard to the application of the process:

(1) No material error will arise in the presence of nitrites in the quantities in which they usually occur.

(2) Iron (in the ferrous or ferric condition), if present in quantities greater than 0.1 part per 100,000, must be removed.

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[1] See preliminary paper, Journal of the Franklin Institute **127**, 61. Ber. d. chem. Gesell. **21**, 3302.

(3) Chlorides, even when present in very small quantities, must be removed.

(4) Carbonate of lime, sulphates of lime, soda, etc., in the quantities in which they ordinarily occur, were not found to influence the determinations.

(5) The presence of easily destructible organic matter, such as albumen, lowers the result; not materially, however, unless present in large excess.

The estimation, briefly described, is made as follows:

Two cubic centimeters of the water to be examined is mixed with 4 cc. concentrated sulphuric acid; the mixture is cooled, and a small quantity of carbazol, dissolved in sulphuric acid, added. If nitric acid is present, the solution will turn green on the addition of the carbazol; and the intensity of the color, by comparison with that produced by solutions of potassic nitrate of known strength, will, within certain limits, indicate the amount of the acid present.

The great majority of waters can be estimated directly without previous concentration, and only a few will need to be diluted. The limits within which the determinations may be safely made are marked by quantities of nitric acid represented by .03 and .40 part N per 100,000. Water containing either less or more nitric acid than indicated by these figures must be concentrated or diluted.

To test the accuracy of the process, a number of solutions were prepared, at my request, containing different quantities of potassic nitrate. In order that my judgment might not be influenced by a knowledge of the amount of nitric acid present, I was kept in ignorance of the strength of the solutions until after the estimations had been completed.

The following are the results obtained:

Nitric Acid expressed as N *in Parts per* 100,000.

Present.	Found.	Error.
.127	.130	+ .003
.078	.075	— .003
.200	.190	— .010
.302	.300	— .002
.290	.290	.000
Average error, ...		.0036

Nitric Acid present in the 2 cc. of Water operated upon, expressed in Decimals of a Gram.

Present.	Found.	Error.
.00001143	.00001170	.00000027
.00000720	.00000675	.00000027
.00001800	.00001710	.00000090
.00002718	.00002700	.00000018
.00002610	.00002610	.00000000
Average error, ...		.000000324

The above results are not selected, but include all the determinations that have been made with solutions of unknown strength, with the object of testing the delicacy of the process. It is to be borne in mind that potassic nitrate *only* was present. Considering the extremely minute quantities operated upon, the accuracy of the above results is very noteworthy.

The following reagents are required:

(1) Concentrated sulphuric acid.
(2) An acetic acid solution of carbazol.
(3) A sulphuric acid solution of carbazol.
(4) Standard solutions of potassic nitrate.
(5) A solution of aluminic sulphate.
(6) A solution of sulphate of silver.

(1) The sulphuric acid, used for all purposes in the process, should be almost entirely free from oxides of nitrogen. It may be readily tested by dissolving in it a small quantity of carbazol. If the solution be at first golden yellow or brown, the acid is sufficiently pure; if it be green or greenish, another and better sample must be taken. It is essential also that the specific gravity of the acid be *fully* 1.84, and it is well to ascertain that this is really the case, as I have found several samples, obtained from sources which are generally thought reliable, to fall considerably below these figures. The acid was in fact worthless for the purpose required. As the success of the process depends upon the proper strength of the acid, I cannot lay too much stress upon this point.

(2) The carbazol used was obtained from Kahlbaum,[1] of Berlin. The acetic acid solution is prepared by dissolving 0.6 gram in about 90 cc. of 99–100 per cent. acetic acid, by the aid of gentle heat. It is allowed to cool, and is then made up to 100 cc. by the

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[1] Kahlbaum's carbazol may be obtained from James W. Queen & Co., Philadelphia.

further addition of acetic acid. The exact strength of this solution is of no material importance to the success of the process, and the above proportions have been selected principally because they are convenient. The solution will probably remain unchanged almost indefinitely; but I cannot speak positively in this respect, as my actual experience extends only over a period of several months. The use of this solution merely facilitates the preparation of that next described, which will not keep, and has consequently to be freshly prepared for each series of determinations.

(3) The sulphuric acid solution of carbazol is easily made in a few seconds, but it is advisable to allow it to stand from one and one-half to two hours before using. It is prepared by rapidly adding 15 cc. of sulphuric acid to 1 cc. of the above described acetic acid solution. This quantity usually suffices in my hands for from two to three nitrate estimations. When freshly prepared it is golden yellow or brown; it changes gradually, however, and in the course of one and one-half or two hours it becomes olive-green. I am not able to say positively to what this change is due, but it seems probable that traces of oxidising agents occur in the sulphuric and acetic acids, and that these, although not present in sufficient quantity to act immediately, gradually bring about the reaction described. The greenish color does not interfere with the process, as might at first be supposed; on the contrary, I have observed that the solution is not sensitive to small quantities of nitric acid until it has undergone the change to olive-green, and it is for this reason that I have advised that it should be prepared about two hours before required for use. This solution may be thoroughly depended on for six hours after preparation. The intensities of color produced by the more concentrated solutions of nitrates after this time, gradually approach to each other and become ultimately the same.

(4) The standard solutions of potassic nitrate are very readily prepared. The solutions which are to be compared directly with the waters examined, may be prepared as required, but if many determinatious are to be made with a variety of waters, it will be found best to prepare a complete series, differing from each other by .02 part nitrogen in 100,000. This series may include solutions containing quantities of nitrogen in 100,000 parts, represented by all the odd numbers from .03 up to .39. It will be found convenient to prepare them in quantities of 100 cc. at a time, from a stock

solution of potassic nitrate (b) which contains .00001 gram nitrogen, or .000045 nitric acid in 1 cc. Each cubic centimeter of this solution, when diluted to 100 cc., represents .01 nitrogen in 100,000, and consequently if it is desired to make a solution containing .35 part nitrogen in 100,000, 35 cc. are taken and made up to 100 cc., and so on. The solution of potassic nitrate (b) is best prepared from a stronger one (a) containing .0001 gram nitrogen to the cubic centimeter, or .7214 gram potassium nitrate to the liter: 100 cc. of (a) made up to one liter gives the solution (b). It is obvious that the series of solutions above described could be made directly from (a), but by first making (b), greater accuracy is secured.

(5) For purposes which will be presently described, a solution of aluminic sulphate is required, containing five grams to the liter. The salt used must be free from chlorine and iron; and the solution should give no reaction when tested, as in the case of a water with carbazol.

(6) The solution of sulphate of silver is required for the removal of chlorine from the water to be examined. It is prepared by dissolving 4.3943 grams of the salt in pure distilled water and making up to one liter. The sulphate is preferably obtained by dissolving metallic silver in pure sulphuric acid. The solution should be tested with carbazol in the same way as will be presently described for water; if perfectly pure, no reaction will be obtained. As sulphate of silver is often prepared by precipitation from the nitrate, it is very apt to contain nitric acid, and consequently, if the source of the salt be not known, this test should on no account be omitted.

Having described the preparation of the reagents, the method of making the determinations may now be considered more in detail. Assuming the water to be free from all substances capable of affecting the accuracy of the results, the process is carried out as follows: Two cubic centimeters of the water is carefully delivered by means of a 2 cc. pipette into the bottom of a test-tube; 4 cc. of sulphuric acid is added, and the solution thoroughly mixed by the help of a glass rod. The test-tube is then immersed in cold water, and when well cooled, 1 cc. of the sulphuric acid solution of carbazol is added, and the whole again mixed as before. The intensity of the color is now observed, and a little experience enables a fairly good opinion to be formed of the quantity of nitric acid present. Suppose that the water is roughly estimated to contain about .15 part nitrogen per 100,000, in such a case, solutions of potassic nitrate containing .11, .15, .19 part nitrogen are selected from the series. Two cubic centimeters are taken from each, and treated side by side with a fresh quantity of the water, precisely as described for the preliminary experiment; the various operations being performed as nearly simultaneously as possible with each of the samples, and under precisely similar conditions. Two or three minutes after the carbazol has been added, the intensity of the color of each is observed. If that given by the water is matched by any of the standard solutions, the estimation is at an end. Similarly, if it falls between two of these, the mean may be taken as representing the nitrogen present in cases in which great accuracy is not required. If this be done, the maximum error will be .02 nitrogen, or .09 part nitric acid per 100,000. If greater exactness be required, or it be found that the color given by the water is either darker or lighter than that given by all the standard solutions, a new trial must be made. In such a case the water must be again tested simultaneously with the solutions with which it is to be compared. This is rendered principally necessary for the reason that the shade of the solutions to which the carbazol has been added is apt to change on standing. Hence it is desirable that the water, and the standard potassic nitrate with which it is to be compared, should have the carbazol added at as nearly the same time as possible. When finally the color falls between that given by any two consecutive members of the standard potassic nitrate series, the estimation may be considered at an end, and the mean of these solutions taken as representing the nitrogen present. The maximum error in this case will be only .01 nitrogen per 100,000 parts, and the mean error slightly more than .005. This degree of accuracy is believed by the author to be quite sufficient for, if indeed it does not exceed the needs of, all ordinary cases of water analysis for sanitary purposes, for which the process was specially devised. If occasionally, however, greater accuracy is desirable, the determinations recorded in the early portion of this paper show that the average error can be reduced to .0036 part nitrogen per 100,000. In this case the standard solutions employed must differ from each other by .01 part nitrogen only. The additional accuracy gained, however, will scarcely repay for the extra time, care and labor required, and even in this case, as will be seen by a reference to the above determinations, the error may amount to .01 part nitrogen per 100,000.

In the course of a great many experiments I have observed, even when the utmost care has been taken, that two solutions, nominally containing the same amount of nitric acid, occasionally give a very slight though distinctly perceptible difference in shade when tested side by side. Whatever may be their cause, such differences are extremely slight, and if proper care be taken, do not materially affect the value of the process.

I cannot too strongly insist upon the necessity of scrupulous cleanliness at all stages of the analysis. The quantity of water operated upon is so small, that if the greatest care be not exercised throughout, sources of considerable error may be readily introduced. The test-tubes used in the process may be conveniently 5 x ⅝ inches in size. They should, of course, be as nearly the same in diameter as possible. It is scarcely necessary to add that they should always be dry when used, and rinsed out carefully with distilled water when put aside.

In comparing the color given by a water with that produced by standard potassic nitrate, it is necessary only to examine the solutions *through* the tubes; differences in shade which can only be detected by looking through the length of the columns of liquid, may be disregarded. It is well to use the same 2 cc. pipette for measuring both the water and the standard potassic nitrate; the effect of any error in graduation is thus neutralised.

I have made experiments to ascertain whether the intensity of color produced is strictly proportional to the nitric acid present, with a view to render the use of a colorimeter possible, and thus to avoid the time and trouble necessary to match the colors given by the waters. The result of these experiments, which were made with a Duboscq instrument, shows conclusively that the changes already referred to in both tint and intensity after the addition of the carbazol, occur more rapidly with the light than with the dark solutions, and hence they are not strictly comparable.

Influence of Nitrites.

It has been already pointed out that nitrous acid behaves similarly to nitric acid in its action on a sulphuric acid solution of carbazol. In order to estimate to what extent its influence would be felt when present in the water to be examined for nitrates, several solutions of silver nitrite were carefully prepared and estimated precisely as if they contained a nitrate.

The results obtained are given in the following table:

Results expressed as N *in* 100,000 *Parts.*

Present as $AgNO_2$.	Found.	Error.	Corrected by deducting one-fifth from amount found.
.10	.12	.02	.096
.20	.25	.05	.200
.30	.37	.07	.296

It will be observed that the error may be very nearly corrected by deducting one-fifth from the amount found. In the presence of nitrates, this correction, of course, will only be possible in cases in which the quantity of the nitrous acid present has been previously ascertained. A correction, however, would be rarely necessary.

Influence of Iron.

Although a solution of ferrous sulphate gives no reaction with carbazol, nitrates are apt to be overestimated in the presence of iron in the ferrous condition. Ferric salts, however, acting like other oxidising agents, are themselves able to give the characteristic green color with carbazol. I have made a number of experiments with solutions of potassic nitrate in the presence of both Fe'' and Fe''' in varying amounts, and have ascertained that if iron be not present in quantities greater than 0.1 part per 100,000, the error will not exceed .01 part in 100,000. The condition of a water with regard to iron may be ascertained sufficiently accurately in a few seconds by the help of ammonic sulphide. As this is a test which should always be made in the examination of water for sanitary purposes, no extra trouble is involved. In a case in which iron is present in large quantities, it can be easily eliminated by rendering the water slightly alkaline, evaporating to dryness, and redissolving the soluble residue in the same volume of pure distilled water as was taken of the water under examination.

Influence of Chlorides.

Chlorides form by far the most serious source of error in this process, by intensifying the action of the nitric acid. If, however, nitrates be absent, chlorides give no reaction with carbazol. Were it not for the fact that the chlorine can be perfectly removed in the space of a very few minutes, the general usefulness of the method would be much restricted. In order to remove the chlorine I use the standard sulphate of silver already referred to, 1 cc. of which, when consumed by 100 cc. of water, is equivalent to one part of chlorine in 100,000 parts of water. Having first determined the chlorine present, by means of a standard nitrate of silver solution of equivalent strength, the exact quantity of sulphate of silver required is known. I proceed as follows: A flask, graduated on the neck at 100 cc. and 110 cc., is filled up to the 100 cc. mark with the water to be examined. The necessary quantity of sulphate of silver is next added, and then 2 cc. of the solution of aluminic sulphate previously described; finally, the contents of the flask are brought up to the 110 cc. mark by the addition of pure distilled water. The whole is shaken up and filtered; the first portion of the filtrate, which will contain any foreign substances derived from the filter paper, is thrown away. The aluminic sulphate, by reacting with the carbonates usually present in the water, and thus giving rise to the precipitation of alumina, facilitates the removal of the precipitated chloride of silver, which otherwise, under the conditions given above, is extremely difficult to separate, and may even still pass through the paper after refiltering many times. When the filtrate is perfectly bright, a portion is tested to make sure that all the chlorine is removed; the estimation is then made precisely as already described, the amount found being increased by one-tenth to compensate for the dilution of the 100 cc. of the water taken to 110 cc.

It is obvious that such a flask as I have described cannot be used in cases in which the chlorine exceeds eight parts per 100,000, unless the sulphate of silver solution be of greater strength than that which I have recommended. Similar methods will, however, readily suggest themselves.

In a preliminary paper[1] published on this process, I mentioned that probably diphenylamine, and other compounds giving similar color reactions in the presence of concentrated sulphuric acid, might be used instead of carbazol for the *quantitative* estimation of nitrates in water. Shortly after this paper appeared, L. Spiegel[2] called attention to a process worked up by him, in which diphenylamine was actually used for this purpose. This is briefly described in the *Zeitschrift für Hygiene*, 1887, 2, 189, and was quite unknown to me. Although differing in detail from that which I have devised, the principle is the same, diphenylamine taking the place of carbazol. Spiegel does not mention any experiments made to ascertain the influence of chlorides, but it is probable that this will be found as considerable as I have found it in the case of carbazol.

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[1] Ber. d. chem. Gesell. **21**, 3302; Journal of the Franklin Institute **127**, 61.

[2] Ber. d. chem. Gesell. **21**, 3568.

THE DISSOCIATION OF THE OXIDES OF ZINC AND CADMIUM IN THE VAPORS OF THEIR RESPECTIVE METALS.

By H. N. Morse and J. White, Jr.

Thirty-four years ago, St. Claire Deville[1] heated some pure oxide of zinc in a porcelain tube, through which a slow current of pure and dry hydrogen was passing. At some distance from the original material he obtained deposits of fine and often large crystals of the oxide. At first he ascribed this transportation of the material to sublimation, and concluded that the oxide is not reducible in a current of hydrogen. But, having learned of the production of metallic zinc in the same way by Rivot, he was led to construct a new explanation for the apparent volatility of zinc oxide in a current of hydrogen. He supposed that the oxide is reduced by the hydrogen, with formation of water and metallic zinc; these then pass along the tube together, until a place having a higher temperature is reached, when the vapor of the metal decomposes the water, with formation of zinc oxide and free hydrogen. This explanation appears to have been accepted as sufficient by all.

On comparing his own apparatus and procedure, by which deposits of oxide only were obtained, with the apparatus and procedure of Rivot, who obtained the metal, it appeared that the latter employed a narrower tube and a much more rapid current of hydrogen. It was afterwards found that, by appropriately varying the width of the tube, the quantity of the oxide, and the rapidity of the current of hydrogen, he could obtain deposits of oxide, of oxide and metal, or of metal and a minute quantity of oxide.

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[1] Ann. chim. phys. (3), **43**, 7 and 477.

Eleven years later, Deville and Troost[1] described an exactly analogous transportation of the sulphides of zinc and cadmium. These were heated in porcelain tubes, in a slow current of pure hydrogen, and, as in the case of the oxide, they were afterwards found some distance away as deposits of hexagonal crystals. To prove that the volatility of the sulphides is only apparent, they were heated to the highest attainable temperature, in a current of hydrogen sulphide. No trace of sublimation could be discovered. The explanation given by the authors is identical in principle with that previously given for the apparent volatility of the oxide. The sulphides were supposed to have been reduced by the hydrogen, with formation of sulphide of hydrogen and free metals. These then passed along together to some other portion of the tubes, where the metallic vapors recovered their sulphur by displacing the hydrogen of the sulphide of hydrogen.

The theory of Deville to explain these interesting phenomena presents certain difficulties. In the first place we must assume a very considerable change in the relative affinities of oxygen and sulphur for hydrogen on the one hand, and the zinc on the other. This would involve large differences of temperature in different parts of the tube; such differences, in fact, as are not likely to have existed under the circumstances of the experiments. Deville speaks of the depositions as having occurred in the hotter portions of the tubes, but we infer from the fact that he obtained deposits which were mixtures of oxide and *metal*, that the places of deposition were certainly not hotter than those from which the metal was first distilled. Again, the sulphide of hydrogen begins to dissociate at 400°, and is destroyed by passing it through a porcelain tube heated to redness. It appears probable, therefore, that the sulphide of hydrogen was not formed at all during the experiments in which the sulphides of zinc and cadmium were transported.

These phenomena are susceptible of quite another explanation than that given by Deville, for which we are able to give some experimental evidence in the dissociation of the oxides of zinc and cadmium in the vapors of their own metals. We suggest that the transportation of the oxide of zinc and the sulphides of zinc and cadmium in a current of hydrogen may have been due to a *dissociation* of the original compounds under the influence of the excess of hydrogen, with reformation at other points where the hydrogen, owing to its deficiency of quantity or lack of temperature, was no longer able to prevent the union of the oxygen and sulphur with the metals. If the chemical elements exert their mutual attractions at other temperatures and under other conditions than those which permit of their actual combination, as we are forced to infer from certain phenomena classed under the heads of *mass* and *catalytic* action, it appears to follow that, when two substances, one a compound and the other something which has an affinity for one of the constituents of the same, are brought together, the stability of the compound must be diminished so that it will dissociate at lower temperatures than in the absence of the substance which exerts an attraction upon one of its constituents. The following three equations will serve to make the meaning of the statement somewhat clearer:

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[1] Ann. chim. phys. (4), **5**, 118.

1. $AB + A = A + A + B.$
2. $AB + B = A + B + B.$
3. $AB + C = A + B + C.$

AB is supposed to represent any compound, *e. g.* ZnO; if now, as in the first and second equations, AB is treated with one of its own constituents in the free state, the added substance, owing to its attraction for the other constituent of the compound, should render the compound less stable, and therefore susceptible of dissociation at lower temperatures.

Again, the stability of the compound should be diminished by the presence of a substance, not in it, but having an affinity for one of its constituents, as represented in the 3d equation.

We have already demonstrated two cases falling under the first equation, by showing that the oxides of zinc and cadmium can be readily dissociated in the vapors of their respective metals.

The third equation represents what we suppose to have taken place in the experiments of Deville and of Deville and Troost. If the oxide of zinc is heated in a current of hydrogen, it is quite possible that, owing to the attraction of the hydrogen for the oxygen, the oxide may be made to break up into its constituents. These would then travel along the tube together, except so far as they separated in consequence of different rates of diffusion, and recombine whenever the attraction of the hydrogen for the oxygen no longer sufficed to keep them separated. Such a failure of the hydrogen to maintain the dissociated condition of the zinc and oxygen might result from a lessening of its relative quantity, or from a lowering of the temperature. The latter appears to be the more probable cause of the reunion of the zinc and oxygen. In the same way the sulphides of zinc and cadmium in a current of hydrogen might be dissociated into their elements, which would volatilise and recombine whenever the conditions permitted.

It is not necessary to suppose the intermediate formation of water in the first case, nor of sulphide of hydrogen in the second. Indeed, the formation of the latter unstable compound appears to be quite improbable.

In order to test experimentally the view here presented, we have selected two of the simplest possible cases falling under the first equation: the dissociation of the oxide of zinc by metallic zinc, and of the oxide of cadmium by metallic cadmium. It has been proved[1] that, under the pressure of the atmosphere, the oxide of zinc does not dissociate below the fusing point of steel, approximately 1400°. But in this work it was decided to experiment, if possible, in a vacuum, because it appeared probable that, should dissociation take place, a portion of the oxygen, owing to its more rapid diffusion, could be isolated, and thus the fact of dissociation demonstrated beyond question. Hence it was necessary to first test the stability of the oxides of zinc and cadmium in a vacuum. This was done by placing them in hard glass tubes closed at one end, and drawing out the open ends so as to properly connect with a Sprengel pump. The tubes were then exhausted, and afterwards heated in a combustion furnace until the glass softened and collapsed from external pressure. During the heating the pump was kept in operation, and a tube filled with mercury maintained over the outlet in order to collect any gas which might be liberated from the oxides. No oxygen was obtained, neither did the oxides exhibit any signs of volatility. It was therefore concluded that they are stable in a vacuum to the highest temperature which we should subsequently employ.

The dissociation of the oxides by means of their respective metals was then effected in the following manner. Hard glass tubes, having a length of about 900 and an internal diameter of about 15 millimeters, were cleansed and closed at one end. The oxides and the metals with which they were to be heated were placed in the closed ends, and any material clinging to the glass above the mixture removed. About one-third of the length of the tube away from the closed end, a deep indentation of the bottom of the tube was made, by softening the glass in the blast-lamp and pressing upon it with a hot triangular file. This was done to prevent any flowing of the metal from the back towards the front end. The open ends were then drawn out and attached by means of rubber tubing, tied with shoemaker's waxed thread, and surrounded by mercury jackets, to a Sprengel pump. The tubes were exhausted to the highest possible degree, and afterwards heated throughout two-thirds of their length, in a combustion furnace. A gas tube filled with mercury was placed over the outlet, after exhaustion had been effected, and the pump kept in operation during the entire experiment. We describe what took place in the case of the zinc oxide and metallic zinc. Very soon after the metal had fused, a fall of several millimeters in the barometer attached to the pump was observed. At the same time gas began to collect in the eudiometer placed over the outlet. On exposing the tube in the furnace to view, it was found that a deposit of yellow oxide had formed in front of the dam. This deposit continued to increase in depth, and to extend itself toward the front end of the tube, until a portion of the zinc had also distilled over and condensed in front of the dam. The oxide which had been deposited near the dam then disappeared, and its disappearance was followed by a rapid increase of the deposition still farther forward. The oxide was thus gradually driven before the distilling zinc, until all of it had been transported to the cool third of the tube lying between the furnace and the pump. In this position it could be seen to fall from above upon the bottom of the tube, in the form of a fine mist of crystals, as long as any zinc remained behind the dam with the oxide not yet dissociated. When all of the zinc had distilled over the dam, and all of the oxide in the heated portion of the tube in front of the dam had been expelled, that is, when metal and oxide were no longer in contact, the deposition at the front end ceased. It could be reinstated, however, by cooling the rear end of the tube, so as to allow the metal to distill back, and then heating again as before. The gas which collected in the eudiometer proved to be pure oxygen. It was measured and determined each time by absorption in an alkaline solution of pyrogallic acid. As would be expected, the collection of the oxygen was most rapid during the early part of the experiment, while the tube was still comparatively free from the vapors of the metal. The evolution continued, however, throughout the whole experiment.

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[1] Morse and Burton, this Journal **10**, 319.

We give below the weights of oxide and zinc taken, the weight of transported oxide collected in the front end of the tube, and the volume of oxygen isolated :

	Weight ZnO.	Weight Zn.	Weight ZnO (transported).	Volume O_2.
1.	25 grams	44 grams	3 grams	7.1 cc.
2.	18	35	8	11.0
3.	31	50	10	not determined

The above results cannot be considered as in any way comparable with one another, because of the impossibility of regulating the temperature so as to secure identical conditions. It still remains to determine in what manner the dissociation is affected by varying the temperature and the relative proportions of oxide and metal.

The phenomena which presented themselves when the oxide of cadmium was heated with metallic cadmium were essentially the same. The oxide collected in front of the dam was driven from that position by the distilling metal, and finally deposited in the cool portion of the tube, in the form of a brown crystalline powder. The quantities of dissociated oxide and of free oxygen obtained were much less than in the experiments with zinc. This is to be ascribed, in part at least, to the lower temperature and greater rapidity of the distillation of the metal away from its oxide. Two experiments were made. In both of them, 20 grams of cadmium and 10 grams of oxide were employed. In the first case, 1½ grams of dissociated oxide and 3.7 cc. of oxygen were obtained; in the second, 2½ grams of oxide and 1.4 cc. of oxygen. There appears to be but one sufficient explanation for the phenomena here described. The atoms of the free metal attract the oxygen in combination to such an extent that the oxide becomes unstable and dissociates. So long as the conditions under which the dissociation was effected are maintained, reformation of the oxide is impossible; that is, no one portion of the metal will be able to appropriate and hold the oxygen in spite of the rest, and the elements will remain in the free state. But as soon as the attraction of the metal for the oxygen becomes sufficiently diminished by falling temperature, or weakened by distribution over a larger number of oxygen atoms, the recombination takes place.

We shall continue to investigate such cases as appear to be suitable tests of the view here presented.

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THE ELECTROLYTIC METHOD APPLIED TO MERCURY-SEPARATION FROM COPPER.

By Edgar F. Smith and Lee K. Frankel.

The electrolytic precipitation of mercury has been successfully performed by different chemists; thus J. B. Hannay[1] recommends a solution of mercury sulphate for this purpose, but gives no quantitative results. F. W. Clarke[2] separated mercury from the solution of its chloride, feebly acidulated with sulphuric acid, by using a current obtained from six Bunsen chromic acid cells. Classen and Ludwig[3] employed a mercury solution rendered slightly acid with nitric acid, and a current affording .5–1.0 cc. electrolytic gas per minute. The time occupied in the deposition, at ordinary temperatures, was 12–16 hours. Hoskinson[4] obtained good results with the nitrate. Smith and Knerr[5] employed a nitrate solution in which there was considerable acid in excess, and with a current yielding 4 cc. electrolytic gas per minute, deposited .1 gram of mercury in forty-five minutes. In all of these methods which permit of the separation of mercury from many other metals, the mercury is thrown out as a mirror-like deposit, and drops of metal are plainly discernible.

We have observed that this metal can be separated without difficulty from solutions containing a large excess of an alkaline cyanide, and with a comparatively weak current. The solution used was the chloride. The conditions, time, strength of current, and results are as follows with mercury alone:

Solution contained Hg.	Found Hg.	Per cent. difference.	Quantity of KCN.	Total dilution.	Time in hours.	Current in cc. OH gas per minute.
.1945 gram.	.1953	+.41	.26 gram.	175 cc.	16	.2 cc.
	.1948	+.14	"	"	"	"
	.1946	+.05	1.3	"	24	"
	.1930	—.77	"	"	"	"
	.1945	...	"	"	12	"
	.1945	...	"	"	"	"
	.1945	...	2.6	"	"	"
	.1944	—.05	.65	"	"	"
	.1942	—1.4	"	"	"	"
	.1956	+.56	"	"	"	"
	.1957	+.61	1.30	"	"	"
	.1948	+.14	"	"	"	"

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[1] Ber. d. chem. Ges. **6**, 270.

[2] Am. Journal of Science **16**, 200; and Ztschr. anal. Chem. **18**, 103.

[3] Ber. d. chem. Ges. **19**, 323.

[4] This Journal **8**, 209.

[5] Ibid.

The deposits in these determinations were compact, rather gray in color, and showed in few cases the drop-like nature so characteristic of mercury.

For washing purposes it was found best to use water only, because when this was followed with alcohol we noticed that the latter detached thin films of metal, causing loss in consequence. The heat of the hand is sufficient to dry the deposit, though a warm iron plate may be used. Some of the deposits were allowed to dry slowly over sulphuric acid. In our experience with about one hundred mercury depositions, we observed but five in which there was a slight oxidation of the metal. This only occurred when a film of water remained in contact for some time with the deposited mercury.

In working with copper solutions, under conditions similar to those mentioned above, we discovered that this metal would not separate until the alkaline cyanide had completely decomposed. We therefore undertook a series of experiments with solutions containing both mercury and copper, hoping to effect their electrolytic separation. This seemed advisable, as the attempts in this direction had thus far not been as successful as might be desired.[1]

Our mercury solution contained the same quantity of metal as in the first experiments. Seventy per cent. of copper was added in each case. The quantity of cyanide varied from .65 gram to 3.9 grams. The total dilution was 200 cc., and the current strength varied from .1–.4 cc. electrolytic gas per minute; time, 6–18 hours. Ten experiments were performed, and notwithstanding the mercury was completely deposited, slight quantities of copper were likewise thrown out of solution.

Thirty additional experiments were made; in each the quantity of mercury was .1945 gram, while the copper varied from 14 to 70 per cent. The quantity of alkaline cyanides varied from 3.9–8.5 grams; total dilution removed 200 cc. The current averaged .4 cc. to 1.2 cc. electrolytic gas per minute; time, 18 hours. The best results were these:

Hg taken.	Hg found.	Diff. in per cent.	Hg found.	Diff. in per cent.
.1945	.1932	— .66	.1936	— .46
	.1920	— 1.28	.1954	+ .46
	.1927	— .92	.1938	— .36
	.1936	— .46	.1923	— 1.13
	.1930	— .77	.1921	— 1.23

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[1] Luckow, Ztschr. anal. Chem. **8**, 24; and Classen, Ber. d. chem. Ges. **17**, 2467, and **24**, 247.

These, as well as the results obtained in twenty experiments made later, seem to indicate that the presence of copper exercises considerable influence upon the precipitation of the mercury, in the way of retarding it. This fact, we think, was confirmed by ten more experiments, in all of which a slight portion of the mercury was retained in solution, notwithstanding the current was increased to 1.2 cc. electrolytic gas per minute and the amount of cyanide considerably reduced. The time of each precipitation was continued through seventeen hours.

Our attention was next directed to ascertaining whether or not a stronger current might be used to throw out the mercury and at the same time leave the copper in solution. The results with mercury alone were:

Hg present.	Hg found.	Diff. in per cent.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.
.1833	.1827	—.27	1.5	200 cc.	2.8 cc.	16
	.1832	—.05	"	"	"	"
	.1834	+.05	"	"	"	"

Using the same quantity of mercury and varying amounts of copper, the results were as follows:

Hg present.	Per cent. of copper present.	Hg found.	Diff. in per cent.	KCN in grams.	Total dilution.	Current in cc. OH gas per minute.	Time in hours.
.1833	1	.1821	—.65	1.5	200 cc.	3.2 cc.	16
	10	.1828	—.27	"	"	"	"
	1	.1821	—.65	"	"	"	"
	14	.1833	...	"	"	"	"
	10	.1821	—.65	"	"	"	"
	5	.1819	—.76	"	"	"	"
	3	.1815	—.98	"	"	"	"
	5	.1834	+.05	"	"	"	"
	3	.1836	+.16	"	"	"	"

The results are recorded in the order obtained, and while the differences in percentage from that required vary from +.05 to —.98, and in six cases out of nine show a deficiency in the mercury, yet a careful qualitative examination of each filtrate failed to detect this metal. The error must, therefore, be ascribed to other causes. It may not be improper to add that these determinations and separations were not always conducted in the same platinum vessels, and further, those used by us ranged in weight from 61–135 grams. Where the quantity of copper exceeded 20 per cent. of the mercury, the results were unsatisfactory.

It is well known that silver can be separated quantitatively from its cyanide solution, but whether its separation from copper could be effected in the same manner as that by which copper and mercury were separated has not been determined. To ascertain this we made forty experiments, ten of which resulted as follows:

Ag present.	Cu present.	Ag found.	Diff. in per cent.	KCN in grams.	Current in OH gas.	Time in hours.	Dilution.	Remarks.
.1223	10%	.1257	+2.78	.5 to 1.0 gram.	1 cc. OH gas per minute.	5 to 20 hours.	200 cc.	Copper precipitated with silver.
		.1299	+6.20					
		.1225	+ .16					
		.1263	+3.20					
		.1257	+2.78					
		.1244	+1.71					
		.1251	+2.20					
		.1242	+1.55					

Later we diminished the quantity of copper, with no better result. On increasing the quantity of cyanide and also the strength of the current, the silver was very notably retarded in its deposition. After carefully repeating the work with no better outcome, we feel justified in saying that the cyanide method cannot be applied in the electrolytic separation of these two metals.

The current employed by us was obtained from storage batteries of the Julien form. Each cell contains 19 plates, each of which is 5¾ inches square. In a long experience with almost every form of battery in electrolytic work, we have not had the same even, steady current for a series of hours as we had with the Julien form, and we recommend it to all engaged in similar experiments.[1]

UNIVERSITY OF PENNSYLVANIA, *April* 13, 1889.

ON THE OCCURRENCE OF LAPACHIC ACID IN BETHABARRA WOOD.[2]

BY WM. H. GREENE AND SAMUEL C. HOOKER.

A few weeks ago we were asked by Mr. A. B. Shipley, of this city, a large importer of Bethabarra wood, to investigate the properties of a yellow substance with which the pores of the wood appear to be filled. So far as we know, the wood is in this country used only for the manufacture of bows and fishing-rods, for which purpose it is admirably adapted on account of its great tenacity and remarkable elasticity.

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[1] See further Ber. d. chem. Gesell. 21, 2892.

[2] Read at the meeting of the Chemical Section of the Franklin Institute, April 16, 1889.

We have been able to learn nothing of the botanical nature of the tree yielding the Bethabarra wood, which is said to be brought from the West Coast of Africa, but we believe that we may venture the opinion that it is a species of Lapacho. The latter is one of the finest ornaments of the sub-tropical hills and plains of South America. Its far-spreading branches are in the spring covered with masses of flowers, red or yellow, according to the variety, so dense that the rays of the sun cannot penetrate them. Its wood is very hard, susceptible of a fine polish, and resists indefinitely the action of moisture.

The considerable cost of the wood made it desirable that some use should be found, if possible, for the refuse.

A few preliminary experiments with the extracted substance showed us that it contained a compound of much scientific interest, and for this reason we felt justified in undertaking the research, independently of any pecuniary result, with which we were not concerned.

On referring to the literature of the subject we found a paper entitled "Preliminary Notice of a New Vegetable Coloring Matter," published by Samuel P. Sadtler and William L. Rowland in December, 1880,[1] concerning the principle of the Bethabarra wood. Aside from analyses, this paper throws but little light on the constitution and properties of the substance, dealing mainly with a comparison of the color reactions of the Bethabarra principle with chrysophanic acid, santalin, haematoxylin and brasilin. The analyses of the authors left them undecided between the formulae $C_{28}H_{29}O_5$ and $C_{22}H_{23}O_4$, and they conclude their paper with a suggestion that a close relationship exists between the Bethabarra principle and chrysophanic acid and haematoxylin.

The Bethabarra wood used in our investigation was mainly in the form of sawdust. This was extracted in quantities of about five kilograms at a time, by percolation with a cold one per cent. solution of crystallised sodium carbonate; the solution was allowed to remain in contact with the wood for several hours, and then drawn off, and the operation was repeated three or four times until the intensity of the deep red color of the extract was much diminished. The liquid was then treated with an excess of hydrochloric acid, and the precipitate allowed to settle, the excess of acid being necessary to insure the rapid separation of the precipitate. The clear liquid was then siphoned off and the precipitate collected on a filter and dried.

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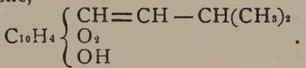
[1] This Journal **3**, 22.

This extract consists of the crystalline principle of the wood, accompanied by a resin, and as both are readily soluble in alcohol, this is not a desirable agent for the first crystallisation as recommended by Sadtler and Rowland. On the other hand we found the resin to be practically insoluble in ether, which freely dissolves the crystalline compound. The dry substance was powdered and shaken with ether in a closed flask; the ether was decanted off as far as possible and fresh ether added two or three times. Before decanting the last time the addition of a few drops of water is desirable, as it causes the resin to agglomerate and adhere to the walls of the flask, thus enabling the solution to be completely poured off without filtration. The ether was then distilled off, and the crystalline mass obtained was thrown on a filter and washed with a little alcohol at the pump. In this way the substance was obtained in a nearly pure condition, one recrystallisation from alcohol yielding an absolutely pure product equal in quantity to at least 0.6 per cent. of the wood employed.

After a brief examination of our substance, we were struck by the remarkable similarity of its properties with those of taiguic acid,[1] which will be found described in Gmelin's Hand-Book **16**, 521, and which has been shown by Paternò[2] to be identical with the greenhartin of Stein[3] and with the lapachic acid of Siewert.[4] Under the latter name, this substance has been the subject of an admirable research by E. Paternò,[5] who from a series of concordant analyses deduced the formula $C_{15}H_{14}O_3$, and was able to assign to it with great probability the constitution of an amylene-oxynaphthaquinone,



$$C_{10}H_4\begin{cases} CH{=}CH-CH(CH_3)_2 \\ O_2 \\ OH \end{cases}.$$

A close examination of the Bethabarra principle established its complete and unquestionable identity with lapachic acid. Its fusing point is 139.5°–140.5°; that of lapachic acid, as given by Paternò, is 138°.

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[1] Comptes rendus **46**, 1152. [2] Gazz. chim. ital. 1879, **9**, 505. [3] J. prak. Chemie **99**, 1.

[4] La République Argentine, par R. Napp, aidé de plusieurs collaborateurs. Ouvrage écrit par ordre du Comité central Argentin pour l'Exposition de Philadelphia. Buenos Ayres, 1876.

[5] Gazz. chim. ital. **12**, 337–392.

We have prepared a number of characteristic salts. That of ammonia is unstable, losing ammonia with great readiness; a dilute solution of this salt deposits crystals of the acid when evaporated, as observed by Paternò with the ammonium compound of lapachic acid.

The silver salt is obtained as a bright red amorphous powder; on analysis we obtained the following figures:

I. 0.2594 gram gave 0.0795 gram silver.

II. 0.2674 gram gave 0.0830 gram silver.

	Found.		Calculated for
	I.	II.	$C_{15}H_{13}O_3Ag$.
Ag	30.65 per cent.	31.04 per cent.	30.95 per cent.

Mean of analyses by Paternò, 30.87 per cent. Ag. Analyses I and II were of compounds prepared separately.

By reducing agents the Bethabarra principle is converted with great facility into a white crystalline substance which rapidly absorbs oxygen from the air, being reconverted into the original compound. This also characterises lapachic acid.

By the action of concentrated sulphuric acid we have obtained a beautiful orange-red, quinone-like, crystalline substance, fusible at 155°–156° and identical with lapachone.[1] Concentrated nitric acid in the cold gives rise to the same substance, as shown by Paternò.

As the unexpectedly rapid result of our research has left us sufficient material to extend our investigations, and as the constitution assigned by Paternò to lapachone is not in accordance with some reactions which we have observed, we propose to make this compound the subject of further study.

PHILADELPHIA, 10*th April*, 1889.

Communications from the Chemical Laboratory of Rutgers College.

XIX.—LECTURE EXPERIMENTS.

By PETER T. AUSTEN.

Simple Apparatus for Showing the Formation of Nitrogen Peroxide, N_2O_4, *from Nitric Oxide*, N_2O_2, *the Solubility of the Former in Water, the Neutrality of Nitric Oxide*, N_2O_2, *and the Acidity of Nitrogen Peroxide*, N_2O_4.

The following simple form of apparatus has worked very satisfactorily in my lecture-room. A large cylinder, best a 1000 cc. glass-stoppered graduated cylinder, is fitted with a double-bored rubber stopper, and provided with two glass-stoppered tubes. The tubes should not be over $\frac{3}{16}$ inch internal diameter, and the long one may, if desired, be drawn to a jet about $\frac{1}{8}$ inch in diameter. The cylinder is filled with water to which has been added enough litmus solution and a drop of caustic soda (not ammonia) to impart to it a deep blue color. The cylinder is next half filled with nitric oxide, N_2O_2, which must be passed through a washer filled with a 10 per cent. solution of caustic soda, in order to remove all traces of acid and the peroxide, N_2O_4, which might otherwise pass over and redden the litmus solution. The rubber stopper and tubes are introduced and pushed in tight. This is done in the deep trough in the lecture-room, care being taken that the cocks are both open, so that the tubes may be entirely filled with water. After the stopper has been inserted, the cocks are closed and the apparatus lifted out of the water. The colorless nitric oxide, N_2O_2, and the fact that it does not affect the litmus, are observed.

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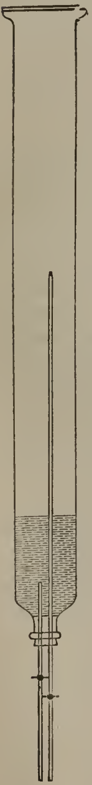
[1] Paternò, loc. cit. 372.



Holding the cylinder in a vertical position with one hand, the cock of the long tube and the cock of the short tube are successively opened with the other. Air enters through the long tube, while the water flows out through the short one. The water is allowed to flow out until the change of color of the gas is apparent. The cock of the short tube and the cock of the long tube are then successively closed, the cylinder held horizontally, and the water allowed to flow to and fro several times. The red peroxide, N_2O_4, dissolves in the water, forming nitric and nitrous acids, and the gas becomes colorless, while the blue color of the solution changes to red. The cylinder is now held vertically, and the ends of both the tubes immersed in water. A cylinder filled to the brim with water is best adapted to this, as it allows the gas-cylinder to be held well up so that it may be easily seen by all. The cock of the long tube is now opened, when the water rushes up and spurts up as a fountain, usually striking the head of the cylinder. When the vacuum has been filled by the entering water, the cylinder is lifted up, thus removing the seal from the tubes, the cock of the short tube is opened, which allows more water to flow out and air to enter. The experiment is then repeated as just described. Four to six repetitions can usually be made before the nitric oxide, N_2O_2, is entirely consumed. The experiment is an unusually effective one.

The apparatus may be made in a simpler and cheaper form by putting in place of the glass stop-cocks on the long tube a four-inch piece of soft rubber tube, clamped at the middle by a pinch-cock, and in the short tube a Krönig valve. This form of the apparatus works in every way as well as the other, but is not so elegant.

Experiments with Gaseous Hydriodic Acid.

After some experimenting, I found the following mixture to yield hydriodic acid gas in abundant quantities: In a six-ounce flask are placed 20 grams of iodine, 5 grams of potassium iodide, 2 grams of red phosphorus, and 10 cc. of water. The whole is well mixed by swirling the flask, and then gently heated. As soon as the action begins, the flask is at once thrust under the cold-water tap until the violence of the action ceases, which occurs in a few seconds. The mixture at once ceases to evolve the gas, but on heating will evolve a large amount, the evolution ceasing as soon as the heat is removed. It is well to pass the gas through an empty Silliman washer, in order that any of the liquid which may distill over may deposit. As a rule, if the heating is too violent, no distillation will take place till toward the end. Vessels can be easily filled with the gas by displacement, the level of the gas being ascertained by introducing a lighted wax lamplighter.

Potassium chlorate placed in an iron deflagration-spoon and heated to boiling, and introduced into a jar of the gas, takes fire and burns with a large red flame, forming clouds of iodine gas and crystals. The sides of the jar become rapidly coated with a deposit of iodine crystals. The reaction is, of course, simply a flame of oxygen in hydriodic acid.

Magnesium.—I was in hope that magnesium would take the iodine away from hydriodic acid, but it does not. A piece of ribbon, when ignited and in full blaze, was dropped into the bottom of a cylinder filled with the gas. It continued to burn for an instant, and was then extinguished. There was, of course, some dissociation of the hydriodic acid.

Sodium, heated red hot and burning, was introduced into a cylinder of the gas, but behaved like magnesium.

Nitrous oxide.—The experiment is best performed by placing a cylinder of the hydriodic acid gas on a cylinder of the nitrous oxide, drawing the glass covers and allowing the gases to mix. A white cloud forms which gradually becomes reddish. Drops of red liquid collect at the bottom, and soon the tubes become filled with a cloud of minute iodine crystals, which gradually deposit on the sides. The red liquid is a solution of iodine in hydriodic acid, and soon deposits crystals of iodine. The water formed by the reaction dissolves some of the hydriodic acid, and this solution dissolves some of the iodine set free. The liquid gives off ammonia when treated with caustic alkali. The reaction appears to be $N_2O + 12HI = 2NH_4I + H_2O$.

The gradual separation and deposition of the iodine makes an interesting phenomenon. The presence of ammonia in the deposited liquid should be demonstrated.

Nitric acid gas, evolved from a mixture of granulated potassium nitrate and sulphuric acid in a small flask, and allowed to issue from a bent-up glass tip having an orifice of about one-eighth of an inch in diameter, takes fire when introduced into the gas, and burns with a fine red flame tipped with a halo of violet iodine gas and a cloud of minute iodine crystals. The sides of the vessel soon become coated with a deposit of iodine crystals.

Chlorine gas, evolving from the apparatus just described, takes fire when introduced into the hydriodic acid gas, and burns with a fine red flame resembling the preceding phenomenon. The stream of chlorine should be rapid, else no flame will be obtained, and only the separation of iodine described by Heumann will be obtained.

Sulphur dioxide makes an effective experiment, and one which is particularly appropriate in demonstrating a chemical change between gases. The cylinder full of hydriodic acid gas is placed on the one containing sulphur dioxide and the glass covers drawn. The colorless gases mix, flashing out deep red, and the sides of the cylinders are at once covered with a deposit of iodine crystals.

THE ESTIMATION OF THE TOTAL ORGANIC NITROGEN IN WATER BY THE KJELDAHL PROCESS.

By Henry Leffmann and William Beam.

Chemists will note with much satisfaction, through the recent communication of Messrs. Drown and Martin,[1] the successful application of the Kjeldahl method to the determination of the total organic nitrogen existing in waters. The so-called albuminoid ammonia process has never been more than a relative determination, and the estimation by the usual combustion method does not seem to be susceptible of general employment in this field. For the benefit of those unfamiliar with the article in question, we present the following abstract:

500 cc. of the water are poured into a round-bottomed flask of about 900 cc. capacity, and boiled until 200 cc. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask, after cooling, is added 10 cc. pure concentrated sulphuric acid. After shaking, the flask is placed in an inclined position on wire gauze, and boiled cautiously in a good drawing hood until the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a little powdered potassium permanganate added until, on shaking, the liquid acquires a green color. If the color is purple instead of green, it shows that the water has not been all driven off. After cooling, 200 cc. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 cc. of sodium hydroxide (200 grams per liter). The flask is connected with a condenser, shaken to mix the contents, and distilled. The first 50 cc. are condensed in very dilute hydrochloric acid free from ammonia. The total distillate is made up to 250 cc., mixed, and 50 cc. taken and nesslerised. A correction for the nitrogen in the chemicals used is made by means of a blank experiment. From the experiments made, Drown and Martin conclude that the nitrates and nitrites do not interfere with the accurate determination of the organic nitrogen, the error which might otherwise be caused disappearing under the conditions of great dilution which exist in natural waters.

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[1] Technology Quarterly 2, 3.

Numerous observations have established the fact that the organic matter of water is susceptible of decomposition or volatilisation by simple boiling, often in such a manner that a notable proportion of the nitrogen is lost. It appeared, therefore, in experimenting on this process, that it would be advantageous to add the acid at once, and thus obtain the nitrogen existing as organic matter and also in ammonium compounds, estimating that existing in the latter in a separate sample by direct nesslerising without distillation; the calcium and magnesium which would otherwise interfere with the color reaction being removed by the addition of sodium carbonate and hydroxide, according to the suggestion of Morgan. The same principle can be extended to the determination of the ammonium formed by the sulphuric acid. Instead of distilling the liquid after rendering it alkaline, a little sodium carbonate may be added, allowed to stand, filtered, and the filter nesslerised. In this way the troublesome distillation is avoided. The procedure is as follows:

Reagents required.—Concentrated sulphuric acid as free as possible from nitrogen; that which we used was of the same make (Baker & Adamson) recommended by Drown and Martin, and contained a similar proportion of nitrogen (.05 mgm. in 10 cc.).

Sodium hydroxide free from ammonium.—100 grams of caustic soda are dissolved in about a liter of water, boiled down to about half its bulk in an open vessel, then diluted to one liter with water free from ammonium.

Sodium carbonate free from ammonium.—200 grams pure sodium carbonate are dissolved in a liter of water, and the solution boiled briskly until several hundred cc. have been evaporated.

Determination of nitrogen existing as ammonium.—200 cc. of the water are placed in a stoppered bottle, 2 cc. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of cotton in a funnel. This should be washed several times with the ammonium-free water. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 cc. of the liquid has passed through it is nesslerised. If the ammonium present is very small in quantity, a rather long and narrow tube should be used for observing the color.

Estimation of total organic and ammoniacal nitrogen.—500 cc. of the water are placed in the round-bottomed flask, 10 cc. of concentrated sulphuric acid added, and the mixture boiled down until the water is driven off and the acid is colorless or pale yellow. The potassium permanganate is then added as above, but after the green color is obtained the flask is reheated until the liquid becomes colorless; this requires but a few minutes. After cooling, 50 cc. of water are added, and then a slight excess of the sodium hydroxide solution; about 150 cc. will be required. 2 cc. of sodium carbonate solution are then added to make sure of the precipitation of the calcium and magnesium, though this is perhaps not necessary, since the caustic soda usually contains more than sufficient carbonate for this purpose. The liquid is cooled by immersing the flask in cold water, made up to 250 cc., transferred to a stoppered bottle and allowed to stand for about an hour, or until the greater portion of the precipitate has subsided. The clearer portion of the liquid is then drawn off with a pipette and run through the cotton-plug filter described above. The filtrate is perfectly clear and colorless. An aliquot portion is taken and nesslerised. We prefer to use 100 cc. and dilute to 200 cc., using rather larger glasses than are commonly employed. Drown and Martin have noted that the addition of potassium permanganate to the concentrated acid is not essential, and merely employ it as a precautionary measure. With the method detailed above, however, it will be found that unless it is used, the nesslerised liquid has a yellowish instead of brown color, and is more difficult to match. A blank experiment is to be made with the reagents used, to determine the amount of the nitrogenous impurity.

We have made trials of the method with various nitrogenous bodies of known composition, and have invariably obtained the theoretical quantity of nitrogen. As an illustration of the trustworthiness of the method the following is given: A sample represented to be pure metadiamidobenzene was purified by recrystallisation, and a solution containing one milligram—equivalent to .000259 nitrogen—added to 500 cc. water and treated as above. Only .000155 nitrogen was obtained. The experiment was repeated four times with some slight modifications of the process, but with almost precisely the same result. On examination it was found that the material used was in reality metadiamidobenzene dihydrochloride, and contained therefore .000154 nitrogen.

The following are a few of the results obtained with natural waters, and a comparison with the results by the distillation method.

PARTS PER MILLION.

Modified Process.

	Nitrogen.		
	In NH_4.	Organic.	Total.
Water, already impure, to which decomposing urine was added,	0.97	2.34	3.31
Pump-well in densely populated district, ...	0.24	0.56	0.80
Cellar water—impure, ...	0.17	0.56	0.73

Drown and Martin's Process.

	Nitrogen.			
	In Free Ammonia.	Organic.	Total.	Lost by Boiling.
Water, already impure, to which decomposing urine was added,	1.25	1.82	3.07	0.31
Pump-well in densely populated district, ...	0.33	0.38	0.71	0.09
Cellar water—impure, ...	0.23	0.41	0.64	0.09

In uncontaminated waters much less difference, and sometimes none, was noticed between the results by the original and the modified process.

The figures show conclusively, we think, even if there were no other observations on the point, that it is not safe to estimate the ammonium in the water by distillation, nor to boil the water previous to the estimation of the organic nitrogen.

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REVIEWS AND REPORTS.

RECENT SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.

The carbohydrates constitute one of the most interesting groups of compounds in organic chemistry. In recent years these valuable and important substances have been the subject of many thorough investigations, a vast amount of knowledge concerning them has been accumulated, and the chemical characters of the individual members of the group have become more and more clearly defined. In spite of all this, however, the attainment of the ultimate objects of chemical research, namely, the determination of their molecular constitution and their synthetical preparation, seemed, until a short time ago, as remote as ever. A very important advance has been made recently in this direction. The first steps in the synthetical preparation of the carbohydrates have been successfully taken by Emil Fischer and his co-workers of Würzburg. A synthetical sugar of the hexane series has been prepared from compounds containing a smaller number of carbon atoms. The new sugar has the composition represented by the formula $C_6H_{12}O_6$. It possesses a sweet taste and has the characteristic properties of the natural sugars, dextrose, levulose, and galactose, and like them it undergoes fermentation when mixed with yeast. It only differs from the natural sugars in being optically inactive, that is, its solution does not turn the plane of polarised light. In short, the synthetical sugar appears to bear the same relation to dextrose and levulose that racemic acid bears to dextro- and levo-tartaric acids.

Fischer's success in this field of work has no doubt been largely due to the use which he has made of phenyl-hydrazine as a means of studying the sugars. This compound was discovered by him in 1875, and is obtained by the reduction of diazo-benzene compounds. It has the power of reacting with the sugars, and indeed with all substances containing an aldehyde or ketone group. With the sugars it forms insoluble crystalline compounds, and in the case of some sugars the phenyl-hydrazine compounds are the only derivatives which can be obtained in the crystalline condition. Briefly stated, phenyl-hydrazine has become an invaluable reagent for the detection and identification of the known sugars. By means of it new sugars, prepared by synthetical processes, can be isolated and studied, and furthermore, thanks to the ingenious experiments of Fischer, sugars of one class, of which dextrose is a type, can be transformed into the isomeric class, of which levulose is a representative.

Action of Phenyl-hydrazine upon Sugars.

When phenyl-hydrazine is brought in contact with substances containing the aldehyde or ketone group, a compound called a *hydrazone* is formed. Thus with aldehyde the following reaction takes place:

$$\underset{\text{Aldehyde.}}{CH_3CHO} + \underset{\text{Phenyl-hydrazine.}}{H_3N_2C_6H_5} = H_2O + \underset{\text{Ethylidene-phenyl-hydrazone.}}{CH_3C(N_2HC_6H_5).}$$

In a similar way, as has been shown in this Journal,[1] phenyl-hydrazine reacts with dextrose, and dextrose-phenyl-hydrazone is formed:

$$\underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Phenyl-hydrazine.}}{H_3N_2C_6H_5} = H_2O + \underset{\text{Dextrose-phenyl-hydrazone.}}{C_6H_{12}O_5(N_2HC_6H_2).}$$

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[1] This Journal **9**, 239.

Analogous hydrazones are obtained from other sugars. As a rule, they are colorless crystalline compounds, and they are precipitated in the cold by bringing together concentrated solutions of the sugar and of phenyl-hydrazine.[1] If, however, dilute solutions of the sugar and the hydrazine be heated to the temperature of the water-bath, then the reaction goes further; the hydrazone which is first formed is acted upon by more phenyl-hydrazine, and a derivative of the sugar containing two residues of the hydrazine, called an *osazone*, is formed. For example, phenyl-glucosazone is formed according to the equation:

$$\underset{\text{Glucose-phenyl-hydrazone.}}{C_6H_{12}O_5(N_2HC_6H_5)} + \underset{\text{Phenyl-hydrazine.}}{2N_2H_3C_6H_5} =$$

$$\underset{\text{Phenyl-glucosazone.}}{C_6H_{10}O_4(N_2HC_6H_5)_2} + C_6H_5NH_2 + NH_3 + H_2O.$$

Similar osazones may be obtained from other sugars. A study of their properties has shown that they are a class of stable substances. They possess a bright yellow color, and on account of their marked power of crystallisation they can be readily obtained in a state of purity. They are insoluble in water, but dissolve in boiling alcohol. As both dextrose and levulose give the same osazone when treated with phenyl-hydrazine, Fischer has given this compound the name phenyl-glucosazone. It crystallises in the form of yellow needles, which melt at 204°. It has the power of reducing Fehling's solution. So readily is this compound formed that even minute quantities of glucose can be detected by means of phenyl-hydrazine. It is only necessary to mix the solution supposed to contain the sugar with an acetic acid solution of phenyl-hydrazine and to heat on the water-bath; if sugar is present, a bright yellow crystalline precipitate will be formed.[2] In a similar manner other osazones are prepared from other sugars, and, owing to their insolubility and great crystallising power, they have become a valuable means of detecting and identifying the sugars. The following is a table of the melting points of the osazones which have thus far been prepared:

Glucosazone,	$C_{18}H_{22}N_4O_4$,	m. p.	204°	from	dextrose. levulose.
Galactosazone,	"	"	193°	"	galactose.
Sorbosazone,	"	"	164°	"	sorbose.
Xylosazone,	"	"	160°	"	xylose.
α-Acrosazone,	"	"	204°	"	α-acrose.
β- "	"	"	148°	"	β- "
Rhamnosazone,	$C_{18}H_{22}N_4O_3$	"	180°	"	isodulcite.
Arabinosazone,	$C_{17}H_{20}N_4O_3$	"	158°	"	arabinose.
Erythrosazone,	$C_{16}H_{18}N_4O_2$	"	167°	"	erythrose.
Lactosazone,	$C_{24}H_{32}N_4O_9$	"	200°	"	milk sugar.
Maltosazone,	$C_{24}H_{30}N_4O_8$	"	191°	"	maltose.
Glycerosazone,	$C_{15}H_{16}N_4O$	"	131°	"	glycerose.

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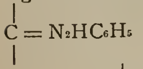
[1] Ber. d. chem. Ges. **20**, 824.

[2] Ber. d. chem. Ges. **22**, 90. Best method of conducting the test.

Cane sugar is inverted by the action of phenyl-hydrazine, and glucosazone, m. p. 204°, is obtained.

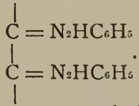
A study of the action of phenyl-hydrazine upon other substances heretofore classed with the glucose group has shown that some of these substances belong to other classes of compounds. Thus inosite, dambose, and scyllite, although they possess the same formula as the glucoses, do not react with phenyl-hydrazine, nor do they reduce Fehling's solution, consequently they are no true carbohydrates. Kiliani[1] has shown that arabinose has the formula $C_5H_{10}O_5$; this fact has been confirmed by a study of the behavior of the compound with phenyl-hydrazine.[2] Mannitose[3] was found to be identical with levulose, while phlorose[4] was identical with dextrose; crocose,[5] on the other hand, was found to consist of a mixture of dextrose with another sugar, the nature of which has not yet been determined. Quercite is an aromatic compound, while isodulcite,[6] $C_6H_{14}O_6$, hitherto regarded as a hexacid alcohol, isomeric with dulcite and mannite, was found to be a sugar belonging to the arabinose group.

In regard to the constitution of the hydrazones and the osazones of the sugars, it seems very probable, from all that is known in regard to these compounds, that in the hydrazones the group



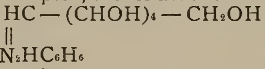
$-\overset{|}{\underset{|}{C}}=N_2HC_6H_5$

is present, while the group characteristic of the osazones is



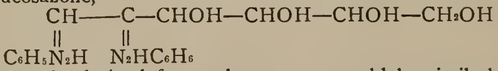
$$\begin{array}{l} | \\ C=N_2HC_6H_5 \\ | \\ C=N_2HC_6H_5 \\ | \end{array}$$

. If then Kiliani's[7] formulas for dextrose and levulose be accepted, the formula for dextrose-phenyl-hydrazone[8] would be



$$\begin{array}{l} HC-(CHOH)_4-CH_2OH \\ \| \\ N_2HC_6H_6 \end{array}$$

and for glucosazone,[8]



$$\begin{array}{ccl} CH & \text{——} C & -CHOH-CHOH-CHOH-CH_2OH \\ \| & \| & \\ C_6H_5N_2H & N_2HC_6H_6 & \end{array}$$

The compounds derived from other sugars would be similarly constituted. It was also observed that the hydrazine derivatives of the natural sugars are optically active, that is, have the power of turning the plane of polarised light.

Transformation of the Osazones into Sugars.—It is then an easy matter, by the methods described, to change a sugar into its corresponding hydrazone or osazone, and these compounds, as has been pointed out above, are one of the best means of detecting and identifying the known sugars, as well as of isolating new members of the series. A method of bringing about the reverse change, that is, of transforming a hydrazone or an osazone into sugar, is also very desirable. For if by synthetical processes a new sugar should be made which could be detected by the phenyl-hydrazine reaction, then the problem would still remain of converting the osazone into the sugar itself. This problem, which proved to be a most difficult one, has also been successfully solved by Fischer.

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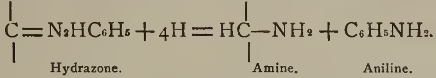
[1] Ber. d. chem. Ges. **20**, 339. [2] Ibid. **20**, 825. [3] Ibid. **20**, 826. [4] Ibid. **21**, 988.
[5] Ibid. **21**, 988. [6] Ibid. **21**, 2173. [7] Ibid. **18**, 3066; **19**, 221, 767, 1910. [8] Ibid. **20**, 821.

The following method was used for decomposing the hydrazones.[1] Treated with cold concentrated hydrochloric acid they are dissolved, and on warming, crystals of phenyl-hydrazine hydrochlorate separate, and the sugar remains in the solution. The decomposition of the hydrazones was effected in still another way.[2] When treated with zinc dust and acetic acid they are converted into amines and aniline, according to the general equation:[3]

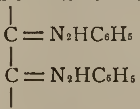


$$\underset{\text{Hydrazone.}}{\overset{|}{\underset{|}{C}}=N_2HC_6H_5} + 4H = \underset{\text{Amine.}}{H\overset{|}{\underset{|}{C}}-NH_2} + \underset{\text{Aniline.}}{C_6H_5NH_2}.$$

The amines are then converted into the corresponding hydroxyl derivatives by the action of nitrous acid.

The transformation of osazones into sugars did not take place so readily as in the case of the hydrazones. The first method employed by Fischer was the same in principle as that which has just been described, namely, reduction with nascent hydrogen, and treatment of the base which is thus formed with nitrous acid. Thus, when phenyl-glucosazone was reduced, a base having the formula $C_6H_{13}NO_5$,[4] and called isoglucosamine, was obtained, and further treatment of this base with nitrous acid converted it into levulose.

It is possible, therefore, to transform dextrose into levulose. The former sugar, by the action of phenyl hydrazine, is converted into glucosazone; the glucosazone, by reduction, yields isoglucosamine, and the latter compound, under the influence of nitrous acid, is transformed into levulose.

The yield of sugar by this method was far from being a satisfactory one, and much better results were obtained in the following way: The osazone was dissolved in cold fuming hydrochloric acid. A dark red-colored solution was formed, which, after standing for some time, gave a deposit of crystals of phenylhydrazine hydrochlorate, and from the solution a compound was obtained which differed from the osazone in having, in place of the group  $\begin{array}{l} | \\ C=N_2HC_6H_5 \\ | \\ C=N_2HC_5H_5 \\ | \end{array}$ of the osazone, the double ketone

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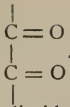
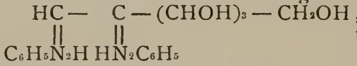
[1] Ber. d. chem. Ges. **20**, 824. [2] Ibid. **20**, 825. [3] Ibid. **19**, 1925. [4] Ibid. **19**, 1920.

group[1] 

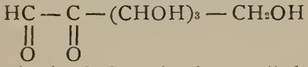
$$\begin{array}{c} | \\ C=O \\ | \\ C=O \\ | \end{array}$$

. As the method was found to be a general one and applicable to all osazone, the new class of compounds thus obtained were called *osones*. Thus from glucosazone, having the formula



$$\begin{array}{ll} HC- & C-(CHOH)_3-CH_2OH, \\ \| & \| \\ C_6H_5N_2H & HN_2C_6H_5 \end{array}$$

the compound



$$\begin{array}{llll} HC- & C- & (CHOH)_3-CH_2OH \\ \| & \| & \\ O & O & \end{array}$$

, called *glucosone*,[2] was obtained. It has also been called oxyglucose, because it may be regarded as an oxidation product of both dextrose and levulose. When treated with nascent hydrogen the osones are converted into sugars.[3] Glucosone, when reduced with zinc dust and acetic acid, was converted into levulose. A much larger yield of sugar was obtained by this method than by the one first described, and it has been successfully employed in converting other osazones into sugars. The following sugars have been prepared from osazones:[4]

Levulose	from	Glucosazone,
Galactose	"	Galactosazone,
Sorbose	"	Sorbosazone,
Lactose	"	Lactosazone,
Maltose	"	Maltosazone,
Arabinose	"	Arabinosazone,
Isodulcite	"	Rhamnosazone,
α-Acrose	"	α-Acrosazone.

In all these cases the transformation took place quite readily. More difficulty was experienced in the case of osazones containing less oxygen, as, for example, erythrosazone and glycerosazone.

As each osazone, by the action of hydrochloric acid, is converted into an osone, and as the latter compounds are closely related to the sugars, it is interesting to note that they readily react with phenyl-hydrazine, and the original osazone is regenerated. Thus glucosone, like dextrose and levulose, with phenylhydrazine gives glucosazone. Like these sugars, it also has the power of uniting with hydrocyanic acid, and, by appropriate treatment, levulinic acid and furfurol may be obtained from it. As the reduction of glucosone converts it into levulose, another method of passing from dextrose to levulose, better than the one first discovered, is to convert the dextrose into glucosazone, to treat this with concentrated hydrochloric acid and thus obtain glucosone, and then to reduce the latter compound with nascent hydrogen. In fact, the method is a general one for changing all natural sugars containing the aldehyde group into the isomeric sugars having the ketone group.

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[1] Ber. d. chem. Ges. **21**, 2631. [2] Ibid. **22**, 87. [3] Ibid. **22**, 94. [4] Ibid. **22**, 87.

Synthetical Experiments.—As the sugars may be regarded as aldehyde and ketone alcohols obtained by the partial oxidation of the hexacid alcohols, it was natural to apply the phenyl-hydrazine reaction to the oxidation products of other poly-acid alcohols, to determine whether compounds analogous to the sugars are not formed when these substances are oxidised. It had long been known that when glycerin is oxidised, a liquid possessing the power of reducing Fehling's solution is obtained. By oxidising glycerin with nitric acid and treating the oxidation product with phenyl-hydrazine, Fischer[1] obtained a beautiful crystalline osazone, which was found to have the formula $CH_2OH - CN_2HC_6H_5 - HCN_2HC_6H_5$, and which had undoubtedly been formed from glycerin aldehyde, or the isomeric compound, dioxyacetone. In a similar manner the compound $C_4H_6O_2(N_2HC_6H_5)_2$ was obtained from the oxidation products of erythrite, while from dulcite a compound isomeric with glucosazone was obtained. A study of these derivatives showed that they belong to the class of osazones, and they were named accordingly. Thus the one obtained from glycerin was called glycerosazone, while the one from erythrite was called erythrosazone; the former melts at 131°, the latter at 167°. Mannite[2] was also oxidised with nitric acid, and among the oxidation products, besides levulose, a new sugar, called *mannose*, was discovered. A careful study of mannose has shown that it has the same constitution as dextrose, and that the isomerism can only be explained by the Van't Hoff and Le Bel hypothesis.

The preliminary experiments on the oxidation of glycerin indicated that the immediate oxidation product, glycerose, consists either of glycerin aldehyde or dioxyacetone, or of a mixture of both. The attempt was next made to prepare glycerin aldehyde from bibrom-acroleïn. The latter substance was treated with dilute baryta water, and a soluble compound, having strong reducing properties and resembling the aldehyde alcohols, was obtained. Many attempts were made to isolate this substance, because it was hoped by means of it to effect the synthesis of a sugar; but it was only by means of the phenyl-hydrazine reaction that trustworthy results were obtained. From the decomposition products of bibrom-acroleïn an osazone of the hexane series, having the formula $C_{18}H_{22}N_4O_4$,[3] was obtained. This synthetical compound, called "acrosazone," to indicate that it had been formed from acroleïn, showed the greatest resemblance in properties to glucosazone. It melts at the same temperature, namely, 205°, and in appearance can scarcely be distinguished from it. At the same time a small quantity of an osazone, isomeric with the one just described and melting at a lower temperature, was found. To distinguish between the two, the former was called α-acrosazone, the latter β-acrosazone. The striking similarity in properties of α-acrosazone and glucosazone indicated that the former was derived from a compound having the formula $C_6H_{12}O_6$, and that this carbohydrate must have been formed from the acroleïn bromide by some such reaction as the following one:

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[1] Ber. d. chem. Ges. **20**, 1088. [2] Ibid. **21**, 1805, and **22**, 365. [3] Ibid. **20**, 1088.

$$2C_3H_4Br_2O + 2BaO_2H_2 = C_6H_{12}O_6 + 2BaBr_2.$$

To obtain the new compound, which appeared to be a sugar, from α-acrosazone, the latter substance was reduced with nascent hydrogen, and the amine thus formed was treated with nitrous acid. A substance possessing all of the ordinary properties of the sugars was obtained. The yield was so small, however, that not sufficient of the compound was obtained for a more detailed study of its properties.

To obtain larger quantities of the α-acrosazone, and so of the synthetical sugar, glycerin was oxidised with bromine in alkaline solution.[1] The oxidation product, called glycerose, was mixed with dilute alkali and allowed to stand four or five days. The object of this procedure is to bring about a condensation of the compounds contained in the glycerose. Phenyl-hydrazine was thereupon added to the liquid, and a precipitate consisting of α- and β-acrosazone was formed. The α-acrosazone was readily separated from the β-compound by means of acetic ether. For the purpose of obtaining the new sugar from α-acrosazone, the second method mentioned above, and which by this time, in the course of the investigations, had been found to give good results in the conversion of glucosazone into levulose, was employed. Concentrated hydrochloric acid transformed the α-acrosazone into a compound almost identical with glucosone in properties. This substance, called α-acrosone, like glucosone, combines with orthotoluylenediamine and forms a crystalline compound, and when boiled with hydrochloric acid it yields levulinic acid. It reacts with phenyl-hydrazine, and the original α-acrosazone is regenerated. Heated with water in a sealed tube to a high temperature, furfurol is formed. Glucosone when reduced is converted into levulose, so the α-acrosone when treated with zinc dust and acetic acid is converted into a compound $C_6H_{12}O_6$, called *acrose*, which in all of its properties shows the closest similarity to the natural sugars. It has a sweet taste and reduces Fehling's solution. Its solution when mixed with an acetic acid solution of phenyl-hydrazine gives, at the temperature of the water-bath, an abundant precipitate of α-acrosazone. The aqueous solution of acrose can be readily fermented by means of yeast. Reduction of dextrose and levulose with sodium amalgam converts them into mannite, $C_6H_{14}O_6$. So also reduction of the acrose by the same means gave a compound $C_6H_{14}O_6$ called *acrite*, which in properties showed the greatest resemblance to mannite. The only difference between the acrose, acrosone, acrosazone and acrite, on the one hand, and the corresponding derivatives of dextrose or levulose, on the other, is that while the latter are optically active and rotate the plane of polarised light, the former are optically inactive. That Fischer will succeed in converting acrose into an optically active sugar by zymogenic fermentation seems highly probable.

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[1] Ber. d. chem. Ges. **20**, 3384.

The synthetical sugar acrose is unquestionably a member of the glucose group. As it is formed by the polymerisation of the oxidation products of glycerin, experiments were undertaken for the purpose of determining the nature of glycerose, as these oxidation products are called. It was found that almost pure glycerose could be obtained by the action of bromine vapor upon lead glycerate.[1] It was suspected that the glycerose consisted either of glycerin aldehyde or of dioxyacetone, or of a mixture of both these compounds. That the latter view was the correct one was shown by treating the glycerose with hydrocyanic acid[2] according to Kiliani's method, and saponifying the resulting compounds. Oxyacids were thus formed. One of these, which was present in small quantity, seemed to be identical with erythroglucinic acid; the other, which was the chief product of the reaction, was proved to be the heretofore undiscovered trioxybutyric acid. As the trioxybutyric acid could only have been formed from dioxyacetone, it appears from these experiments that the latter substance is the chief constituent of glycerose, but at the same time there seems to be some of the isomeric glycerin aldehyde present.

Acrose has been obtained by still another method. It was observed by Butterow,[3] afterwards by Tollens,[4] and more recently by Loew,[5] that when formic aldehyde is treated with lime water, a polymerisation product is obtained which has the power of reducing Fehling's solution. Loew has given the substance the name "formose," and he regarded it as a member of the glucose series of sugars. Fischer[6] has recently shown that it is a mixture of several aldehyde or ketone alcohols which can be separated by means of phenyl-hydrazine. He succeeded in isolating α-acrosazone, thus proving that one of the compounds formed by the polymerisation of formic aldehyde is a sugar of the glucose series. This fact is all the more interesting when it is remembered that acrose is closely related to the natural sugars, dextrose and levulose—in fact, appears to be the "inactive" modification of these compounds. At all events, these experiments make Baeyer's theory of plant assimilation appear more probable. According to this theory, glucose is formed in plants by the polymerisation of formic aldehyde, the latter substance being produced in the leaves by the reduction of carbonic acid.

E. H. Keiser.

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[1] Ber. d. chem. Ges. **21**, 2634.
[2] Ibid. **22**, 106.
[3] Ann. der Chem. (Liebig) **120**, 295.
[4] Ber. d. chem. Ges. **15**, 1629.
[5] J. prakt. Chem. (2), **33**, 321; **34**, 51.
[6] Ber. d. chem. Ges. **22**, 359.

NOTES.

A Vexatious Mixture for Qualitative Analysis.[1]

In most of the methods of qualitative analysis, silver is detected in the hydrochloric acid group, and if not detected there, is not sought for further. There are cases, however, in which such a procedure may lead to a failure to detect silver, when the method is carried out by students. The following mixture proves, as a rule, very vexatious to beginners, and even men of experience have fallen under its baneful influence, when asked to test the solution for silver alone.

Concentrated hydrochloric acid is added to a ten per cent. solution of silver nitrate until the silver is all precipitated as chloride and some excess of hydrochloric acid is present. The liquid is then neutralised with strong ammonia, and some excess over the amount required to dissolve the silver chloride is added. Hydrochloric acid is again added until the liquid is acid. The solution now contains the double chloride of silver and ammonia (Faraday), and is not precipitated by hydrochloric acid. It is precipitated by water, however, and the precipitate so formed is redissolved on the addition of hydrochloric acid.

To the solution[2] are now added solutions of tartar emetic, bismuthic nitrate in dilute nitric acid, and cupric nitrate, the resulting turbidity being cleared up after each addition with a little hydrochloric acid. The mixture is then given out for analysis. The student begins by diluting the liquid and gets a white precipitate, which redissolves in an excess of hydrochloric acid to a clear liquid. He ascribes this to the presence of bismuth or antimony, and notes the absence of the hydrochloric acid group. He finds in their proper places antimony, bismuth and copper. He is quite sure that silver is not present, as the absence of a precipitate by hydrochloric acid excludes it. When he finds later on that the original acid solution contains hydrochloric acid in large amounts, since it yields a heavy precipitate with silver nitrate, he is doubly certain, nor can he be blamed for his false inference.

The bismuth is removed with ammonia, and the filtrate precipitated with hydrogen sulphide. The resulting precipitate of copper sulphide and silver sulphide is boiled with dilute sulphuric acid, filtered, and tested for cadmium. None is found. Copper has announced its presence by the blue color with ammonia in making the bismuth test. There is hence no need to examine the precipitate of copper sulphide and silver sulphide. The silver has escaped detection.

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[1] Communication from the Chemical Laboratory of Rutgers College.

[2] This is, of course, but an example of many mixtures that can be made, any of which will make trouble with the mechanical or routine analyst.

If the amount of silver present as double chloride of silver and ammonium is small, and a considerable amount of mercuric chloride is present, and the sulphides are not well washed out, a considerable amount of ammonium chloride will stay in the precipitate. When this precipitate is dissolved in nitric acid, *aqua regia* will be formed, and will convert the silver into the chloride, which, being practically insoluble, will remain with the mercuric sulphide residue, and will hence escape detection altogether, or it will be called lead sulphate, if lead is also present.

The remedy for the first oversight is to test the nitric acid solution of the group sulphides of the fifth group with hydrochloric acid before testing for lead with sulphuric acid. If desired, any lead which goes down as the chloride with the silver chloride, may be separated with hot water. Such a procedure is laid down in some of the small German text-books. The point should not be overlooked, and should be demonstrated in the lecture course; for even an experienced chemist may easily make a mistake in such an unexpected case as this.

The remedy for the second oversight is not as simple as it may appear. To get the student to make satisfactory separations in qualitative analysis is not an easy task. In fact, it is rarely accomplished until after he has had some experience in quantitative work. I believe that better results in the teaching of qualitative analysis would be obtained if the course in analytical chemistry were to begin with a certain number of quantitative analyses of pure substances. Following them should come the study of qualitative analysis; and following this, again, the remainder of the course in quantitative analysis. This is essentially the plan advocated by Dr. Muck of Bochum.

PETER T. AUSTEN.

New Researches proving that the Poisonous Effect of Exhaled Air is not due to Carbon Dioxide.

In a previous paper by Brown-Sequard and d'Arsouval, the relation between exhaled air and certain forms of disease was investigated. In these researches the same writers show that this air contains a poison (either simple or complex) which can produce death even when not directly injected into the blood. The effect of breathing this air was investigated by means of an apparatus, the essential parts of which are as follows:

A series of air-tight metallic cases were connected with one another, and a current of air drawn through the series by means of a suction pump. Into each of these cases was placed a rabbit. The rabbit in the first case thus breathed only pure air; those in the succeeding cases breathed the air which came from the preceding cases, which was therefore more and more contaminated. Young rabbits (from 5 to 7 weeks old) died very quickly, with the exception of those in the first and the second cases. Those in the last two cases sometimes died in 2 or 3 days. If a dying rabbit were removed and placed in pure air, it recovered after 5 to 10 days. With large rabbits the general results were the same, and only differed in regard to the time. There was never more than six per cent. of carbon dioxide in the last of the cases, but it was deemed advisable to prove that this did not cause the death of the rabbits. The air could not be passed through caustic alkali in order to remove the carbon dioxide, for the alkali also destroyed or absorbed the poison. By passing the air through a tube filled with glass beads moistened with strong sulphuric acid, the poisonous matter was destroyed and the carbon dioxide left unchanged. By placing such a tube between the sixth and seventh cases, it was found that the rabbit in the seventh case did not die, thus proving that carbon dioxide was not the cause of the death of the rabbits. In a number of other experiments the authors have shown that air containing a considerable percentage of carbon dioxide (free from hydrochloric acid) can be breathed with impunity by men, rabbits, dogs, etc. They themselves remained for several hours in an atmosphere containing 20 per cent. of carbon dioxide without experiencing the slightest inconvenience.

If the poison contained in exhaled air be absorbed, and the solution injected into an animal, death generally results. The solution may be heated to 100° C. without destroying its properties in this respect, thus showing that its effects are not due to microbes.—(*Comptes rendus*, 1889, **108**, 267).

RUDOLF DE ROODE.

On the Valence of Aluminium.

The subject of the molecular weight of aluminium has again been under investigation, this time by A. Combes. The substance used was the acetyl-acetonate of aluminium, $[Al(C_5H_7O_2)_3]_n$. This was obtained in a very pure condition as a white solid, melting at 193°–194°, and boiling without decomposition at 314°–315° (cor.).

The vapor density was determined by V. Meyer's method, in an atmosphere of pure, dry nitrogen at the temperature of boiling mercury. Two consecutive determinations gave the following figures:

Weight of substance.	Volume of gas.	Temperature.	Barometer.	Tension of aqueous vapor.
0.2105 gram.	15.2 cc.	14.5°	771.5 mm.	12.3 mm.
0.1798	13.1	15	770.9	12.7

Density.		Molecular Weight.	
Found.	Calculated.	Found.	Calculated for $Al(C_5H_7O_2)_3$.
11.27	11.236	325.5	324.5
11.23		324.2	

The volatilisation took place in a very regular manner and without decomposition. After cooling, the substance appeared in perfectly colorless crystals, completely soluble in alcohol. The results of these experiments show, therefore, that the acetyl-acetonate of aluminium is not altered at a temperature of 360° in an atmosphere of nitrogen, and that its vapor density at this temperature (only 45° above its boiling point) corresponds to the formula $Al(C_5H_7O_2)_3$, and not $Al_2(C_5H_7O_2)_6$.—(*Comptes rendus*, 1889, **405**.)

RUDOLF DE ROODE.

The Life of Avogadro.

The following facts of interest concerning the life of Avogadro, about which very little is generally known, are taken from a notice in the *Chemiker-Zeitung* **13**, 17, by Professor Hugo Schiff, of Florence:

Amedeo Count Avogadro, son of the magistrate Filippo Vercellone, was born in Turin, August 9, 1776. He studied jurisprudence at the Turin University, became Doctor of Laws on March 16, 1796, and then held a position under the government until 1806, at which time he began his career as a scientist. In physics he was self-taught, and obtained a subordinate position in the Collegio delle Provincie in Turin, which was then, and still is, a richly endowed department of the Turin University. On Nov. 7, 1809, he became Professor of Physics at the Gymnasium in Vercelli. In 1820 he was elected Professor of Mathematical Physics at the Turin University. Later this chair of instruction was abolished, and Avogadro resumed the practice of law. He was, however, reinstated in his chair through the influence of Charles Albert, and remained at the university until 1850, when he retired on account of old age and ill health. He died in Turin, July 9, 1856, at the age of 80 years.

Avogadro was but little known in Italy and unknown in foreign countries. He shared with Charles Gerhard, who died in the same year, Aug. 19, 1856, the same fate. It was only after death that their great and important contributions to science found recognition.

RUDOLF DE ROODE.

Michel Eugene Chevreul.

This distinguished chemist, whose name has been and will be so familiar to scientists on account of his classic researches on the fats and also on various dye-stuffs—to the world in general on account of his marvellous longevity—has at last shared the common fate of all. He died in Paris, April 9, 1889, at the age of 102 years. Born in Angers on Aug. 31, 1786, he went to Paris in 1803, and in 1806 was appointed Director of Vauquelin's Laboratory and Professor in the Lycée Charlemagne. He also occupied other positions of importance and honor. He was a member of the Academy of Sciences, and never failed to attend its meetings up to his one hundredth birthday, on which occasion he was the recipient of much distinction and honor. Chevreul was a careful observer and faithful student of nature, his work being characterised by its accuracy and thoroughness. The larger part of his researches was upon fats and oils. The principal journals of the day from 1806 to 1876 contained numerous articles from his pen. In 1823, the work on fats and oils which had from time to time appeared in the current journals was arranged in systematic order, and published under the title "Recherches sur les corps gras." It formed a volume rich in valuable information. Few fields of chemistry had been so thoroughly worked out, and these researches formed a great contribution both to science and the arts. Considering the very small advance which had been made in the field of organic chemistry, this work of Chevreul, as well as almost everything which he undertook, showed him to be a man far in advance of his time. Next in importance to his researches upon the fats were those upon various dye-stuffs, the results of which were communicated to the Academy of Sciences of Paris, under the title "Recherches sur la teinture." In this communication he reviewed exhaustively the dye-stuff industry of the day; proposed a theory of complementary and of mixed colors; and again presented to science and art a great contribution. His other researches were of minor importance, yet worthy of careful attention and study. Notwithstanding his great age, Chevreul retained his deep interest in science and kept up with the times to the last.

R. DE R.

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ON THE NATURE AND STRUCTURE OF THE DOUBLE HALIDES.

By Ira Remsen.

In studying modern chemical literature, one cannot fail to be impressed by the fact that the compounds commonly called double salts of the halogens or double halides are generally treated, if treated at all, in a highly unsatisfactory way. Few of them are mentioned, and these are passed over as lightly as possible, but little attempt being made to explain them, or to point out the relations which exist between them and other chemical compounds. Some time ago, while engaged in the preparation of one of my text-books, I made a systematic study of the present state of our knowledge concerning these compounds, and soon reached the conviction that they are simpler than they are commonly held to be. What appears to me to be an entirely satisfactory explanation of them suggested itself; and further investigation showed that the same explanation had already been offered by others. But owing partly, I think, to the fact that the evidence in favor of the explanation has never been fully presented to chemists, it has not been generally accepted. It therefore seems to me desirable to discuss somewhat fully the facts known concerning the formation and existence of the compounds in question. I cannot but believe that a careful consideration of these facts, and of the thoughts which they suggest, will lead to the general acceptance of a conception which hitherto has received but scant recognition.

1. *Number and Formation.*

About four hundred compounds belonging to the general class of double halides have been described, and judging by the great variety of these, it would probably be a comparatively simple matter to add largely to their number, if there were any incentive to their preparation. By far the largest number of those known are formed by the direct combination of a halogen salt of one of the alkali metals with the corresponding salt of some other metal, especially aluminium, chromium, lead, platinum, etc. Many are made by bringing the halogen salts together in strong acid solution; others, like aluminium potassium chloride, $KAlCl_4$ or $AlCl_3.KCl$, by bringing the vapor of one in contact with the other salt in highly heated condition. The corresponding sodium aluminium chloride is, further, manufactured on the large scale by passing chlorine over a highly heated mixture of aluminic oxide, charcoal, and sodium chloride, *when the double salt*, $AlCl_3.NaCl$ or $NaAlCl_4$ *distills over.* Not only do the halogen salts of the metallic or basic elements combine with those of the alkali metals; the halogen compounds of the acidic elements such as sulphur, selenium and tellurium, phosphorus, arsenic, and antimony, silicon, and boron, also combine with the halogen salts of metals. But, just as the halogen compounds of the acidic elements are easily decomposed by water, so also the double salts into which these compounds enter are for the most part easily decomposed by the same agent, so that there are serious difficulties in the way of preparing such compounds in pure condition. Still, a sufficient number has been made to show that the halogen compounds of the acidic elements combine with facility with halogen salts. The evidence appears to show that under proper conditions chlorides combine with chlorides, bromides with bromides, iodides with iodides, and fluorides with fluorides, as readily as oxides combine with oxides, and sulphides with sulphides. Further, it has been shown that *mixed double halides* can be formed. Thus, when antimony trichloride, $SbCl_3$, is brought together with potassium bromide, the salt $SbCl_3.3KBr$ is formed, and there are some other examples of the same kind known, though the number is small. The chief difficulty encountered in making salts of this kind is found in the fact that they must be made in the presence of one of the halogen acids, and this at once exerts an influence on the course of the reaction. For example, in most cases it is impossible to make a double salt containing both bromine and chlorine in a solution containing hydrochloric acid, as the bromide, under the circumstances, is converted into the corresponding chloride, and the double salt formed contains only chlorine.

There are then two difficulties in the way of preparing double halide salts. The first is the ease with which most such compounds are decomposed by water. The second is the ease with which the salt of one halogen is decomposed by the acid of another.

2. *Composition.*

A study of the double halides with reference to their composition reveals an interesting regularity which appears to be of the highest importance in enabling us to judge of their nature. The character of this regularity will be made clear by a consideration of some typical examples. There are few, if any, examples of such salts in which only univalent metals enter. Potassium chloride does not unite with sodium chloride to form a stable compound. Passing, however, to the bivalent metals as magnesium, zinc, beryllium, mercury, copper, lead, tin, etc., we find that their halogen salts form two classes of compounds represented by the following general formulas, in which M^{II} represents a bivalent metal, Hl any halogen, and M^{I} a univalent metal, generally potassium or sodium:

$$(1)\ M^{II}Hl_2.M^{I}Hl \text{ or } M^{I}M^{II}Hl_3,$$
$$\text{and } (2)\ M^{II}Hl_2.2M^{I}Hl \text{ or } M^{I}_2M^{II}Hl_4.$$

Examples of these two classes are the salts represented by the following formulas:

First Class.	Second Class.
$BeF_2.KF$ ($KBeF_3$)	$BeF_2.2KF$ (K_2BeF_4)
$MgCl_2.KCl$ ($KMgCl_3$)	$MgCl_2.2KCl$ (K_2MgCl_4)
$MgBr_2.KBr$ ($KMgBr_3$)	
$MgI_2.KI$ ($KMgI_3$)	
$ZnCl_2.KCl$ ($KZnCl_3$)	$ZnCl_2.2KCl$ (K_2ZnCl_4)
	$ZnCl_2.MgCl_2$ ($MgZnCl_4$)
$HgCl_2.RbCl$ ($RbHgCl_3$)	$HgCl_2.2RbCl$ (Rb_2HgCl_4)
$HgBr_2.KBr$ ($KHgBr_3$)	
$HgI_2.KI$ ($KHgI_3$)	$HgI_2.2KI$ (K_2HgI_4)
$SnCl_2.KCl$ ($KSnCl_3$)	

First Class.	Second Class.
$PbI_2.KI$ ($KPbI_3$)	$PbI_2.2KI$ (K_2PbI_4)
$PdCl_2.KCl$ ($KPdCl_3$)	$PdCl_2.2CsCl$ (Cs_2PdCl_4)
$PtCl_2.RbCl$ ($RbPtCl_3$)	$PtCl_2.2CsCl$ (Cs_2PtCl_4)

The halogen salts of the trivalent elements, as aluminium, iron, antimony, gold, chromium, etc., form three classes of compounds which are represented by the general formulas

(1) $M^{III}Hl_3.M^IHl$ or $M^IM^{III}Hl_4$
(2) $M^{III}Hl_3.2M^IHl$ or $M^I_2M^{III}Hl_5$
and (3) $M^{III}Hl_3.3M^IHl$ or $M^I_3M^{III}Hl_6$.

Examples of these three classes are the salts represented by the following formulas:

First Class.	Second Class.	Third Class.
$BF_3.KF$	$AlF_3.2NaF$	$AlF_3.3NaF$
(KBF_4)	(Na_2AlF_5)	(Na_3AlF_6)
$AlCl_3.KCl$	$BiCl_3.2KCl$	$BiCl_3.3KCl$
($KAlCl_4$)	(K_2BiCl_5)	(K_3BiCl_5)
$AuCl_3.KCl$	$BiI_3.2KI$	$BiCl_3.3NaCl$
($KAuCl_4$)	(K_2BiI_5)	(Na_3BiCl_6)
$AlBr_3.KBr$	$CrCl_3.2KCl$	$CrCl_3.3KCl$
($KAlBr_4$)	(K_2CrCl_5)	(K_3CrCl_6)
$AuBr_3.KBr$	$SbCl_3.2KCl$	$InCl_3.3KCl$
($KAuBr_4$)	(K_2SbCl_5)	(K_3InCl_6)
$CrCl_3.KCl$	$SbF_3.2KF$	$RhCl_3.3KCl$
($KCrCl_4$)	(K_2SbF_5)	(K_3RhCl_6)
$FeCl_3.KCl$	$RhCl_3.2KCl$	$SbF_3.3KF$
($KFeCl_4$)	(K_2RhCl_5)	(K_3SbF_6)

Most of the double halides formed by quadrivalent elements have the general formula

$$M^{IV}Hl_4.2M^IHl \text{ or } M^I_2M^{IV}Hl_6.$$

This is shown in the salts represented by the following formulas:

$PtCl_4.2KCl$ (K_2PtCl_6)
$SiF_4.2KF$ (K_2SiF_6)
$PdCl_4.2KCl$ (K_2PdCl_5)
$PtI_4.2NaI$ (Na_2PtI_6)
$PtBr_4.2NaBr$ (Na_2PtBr_6)
$SnCl_4.2NaCl$ (Na_2SnCl_6)

$TiF_4.2KF$ (K_2TiF_6)
$ZrF_4.2KF$ (K_2ZrF_6)
$GeF_4.2KF$ (K_2GeF_6)

There are a few examples of another class of double halides derived from the halogen salts of quadrivalent elements. These have the general formula

$$M^{IV}Hl_4.M^{I}Hl \text{ or } M^{I}M^{IV}Hl_5.$$

Such are the following :

$SnF_4.KF$ ($KSnF_5$)
$SnF_4.LiF$ ($LiSnF_5$)
$SiF_4.LiF$ ($LiSiF_5$)
$SiF_4.AgF$ ($AgSiF_5$)
$SnF_4.NaF$ ($NaSnF_5$)

And finally there is one representative of another class of the general formula

$$M^{IV}Hl_4.3M^{I}Hl \text{ or } M^{I}_3M^{IV}Hl_7.$$

This is the salt $ZrF_4.3KF$ or K_3ZrF_7.
Salts of the general formula

$$M^{IV}Hl_4.4M^{I}Hl \text{ or } M^{I}_4M^{IV}Hl_8$$

have not been described.

Passing to the quinquivalent elements, there are found a few representatives of five classes of compounds of the following general formulas :

$M^{V}Hl_5.\ M^{I}Hl$ or $M^{I}M^{V}Hl_6$
$M^{V}Hl_5.2M^{I}Hl$ or $M^{I}_2M^{V}Hl_7$
$M^{V}Hl_5.3M^{I}Hl$ or $M^{I}_3M^{V}Hl_8$
$M^{V}Hl_5.4M^{I}Hl$ or $M^{I}_4M^{V}Hl_9$
$M^{V}Hl_5.5M^{I}Hl$ or $M^{I}_5M^{V}Hl_{10}$.

Only two or three examples of the last two classes are known, and these have a somewhat more complicated composition than that represented by the formulas given. The substances in question are :

$AsF_5.KF$ or $KAsF_6$
$AsF_5.2KF$ or K_2AsF_7
$NbF_5.2KF$ or K_2NbF_7
$NbF_5.3KF$ or K_3NbF_8

$PCl_5.AlCl_3$ or $AlPCl_8$
$PCl_5.2SnCl_2$ or Sn_2PCl_9
$PCl_5.SbCl_5$ or $SbPCl_{10}$.

The examples given in the above tables are fair representatives of the whole class of double halides, except that all ammonium salts are omitted. The double halides formed with halogen salts of ammonium are very numerous, and many of them are quite complicated. There are indeed ammonium salts known belonging to all the classes above mentioned, but there are many others which do not belong to these classes. Considering the power of ammonium salts in general to form complex compounds with metallic salts, one cannot avoid the conclusion that there is some power in nitrogen which makes the formation of these compounds possible. The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own. As regards all other double halides, however, the examples chosen are representative. While most of these salts consist of some other halide combined with a halide of an alkali metal, there are those in which, instead of the alkali salt, a salt of calcium, barium, or, in exceptional cases, of some less strongly marked basic element, enters. Such, for example, are the following:

$ZnCl_2.BaCl_2$ or $BaZnCl_4$
$AlF_3.CaF_2$ or $CaAlF_5$
$PtCl_4.BaCl_2$ or $BaPtCl_6$
$PtBr_4.PbBr_2$ or $PbPtBr_6$
$SiF_4.CaF_2$ or $CaSiF_6$.

As will be seen, however, all these salts follow the same law of composition as those which are formed by the halides of the alkali metals. This law may be stated thus:

When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter.

According to this law, double halides of the following general formulas are possible:

$$\mathrm{M^{II}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{II}}\begin{cases}\mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}$$

$$\mathrm{M^{III}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{III}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{III}}\begin{cases}\mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}$$

$$\mathrm{M^{IV}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{IV}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{IV}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{IV}}\begin{cases}\mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}$$

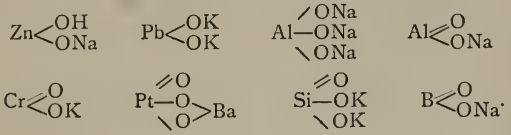
$$\mathrm{M^{V}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{V}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{V}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{V}}\begin{cases}\mathrm{Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}\qquad \mathrm{M^{V}}\begin{cases}\mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\\ \mathrm{Hl.M^{I}Hl}\end{cases}$$

As already shown, representatives of all these classes, except that of the formula $M^{IV}Hl_4.4M^{I}Hl$, are known; and by far the largest number of all the double halides known belong to one or the other of these classes. There are a few which differ from these fundamental forms, but examination shows that they are closely related to these forms. Thus there are compounds of the formulas $2AuCl_3.KCl$, $2AuCl_3.MgCl_2$, $3BiCl_3.2KCl$, etc., but, as will be pointed out further on, the relation between these and the simpler salts is probably similar to that which exists between the salts of the so-called poly-acids and the simpler salts. Certainly the explanation which holds good for the simpler salts is entirely adequate to account for the existence of those of more complex composition.

Finally, there is one exception to the above law known. This is the salt of the composition $CuCl.2KCl$ or $Cu_2Cl_2.4KCl$. While this compound cannot, of course, be ignored, it seems fair, in view of the fact that it is the only exception to the law in nearly four hundred cases, to hope that some explanation will be found for its anomalous composition which will be in harmony with the general law. It should be observed that it is formed from the unsaturated molecule $CuCl$, and this fact may have something to do with the peculiarity of its composition. This point will be referred to again further on.

3. *Analogy between Double Halides and Oxygen Compounds.*

As is well known, many so-called metallic hydroxides, as those of aluminium, chromium, zinc, platinum, and lead, dissolve in the hydroxides of the alkali metals or of the metals of the calcium group, and form salt-like compounds. Several of these have been investigated, and they have been shown to be derived from the more complex hydroxide by the replacement of one or more of the hydrogen atoms by an equivalent number of atoms of the more strongly basic element. Among salts of this kind are the aluminates of sodium and potassium, the chromites, the zincates, the plumbates, etc. The aluminates are, for the most part, derived from the hydroxide $AlO.OH$, which is in turn derived from the normal hydroxide $Al(OH)_3$, by loss of one molecule of water. The chromites are analogous to the aluminates. The zincates are apparently derived from zinc hydroxide by the replacement of one hydrogen atom by an alkali metal. The platinates are derived from the hydroxide $PtO(OH)_2$, which is in turn derived from the normal hydoxide $Pt(OH)_4$, by loss of one molecule of water. The composition of some of the better known compounds of the kind here referred to is represented by the following formulas:



It requires but a superficial examination to show that, with the exception of the zincate, there is perfect analogy between the composition of these compounds and that of the double halides of the same elements. This is clearly shown by placing the formulas of some of the better known compounds of the two classes side by side thus:

K_2PbO_2	K_2PbI_4
$NaAlO_2$	$NaAlCl_4$
$KCrO_2$	$KCrCl_4$
Na_3AlO_3	K_3CrCl_6
$BaPtO_3$	$BaPtCl_6$
K_2SiO_3	K_2SiF_6
$NaBO_2$	KBF_4
$AlPO_4$	$AlPCl_8$
$FePO_4$	$FePCl_8$

This analogy between the composition of the so-called double halides on the one hand and that of the oxygen compounds on the other is general.

While the oxygen compounds or oxygen salts above referred to are generally formed by the action of a hydroxide upon a hydroxide, for the reason that it is more convenient to work with solutions than with dry substances, it is equally true that the same compounds can be made by bringing together the corresponding oxides, and this mode of formation is strictly analogous to that employed in making some of the double chlorides, as, for example, when dry aluminium chloride is heated with dry potassium chloride. Just as these unite to form the compound $KAlCl_4$, so aluminium oxide and potassium oxide unite to form the compound $KAlO_2$.

As regards the formation of double chlorides in solution, it should be remarked that this mode of formation is not strictly analogous to the formation of oxygen salts by bringing together oxides in solution. In the latter case the water generally acts first upon one or both of the oxides, converting them into hydroxides, and these in turn act upon each other. When a chloride is treated with water, however, there may be decomposition and conversion into the hydroxide either partial or complete. In the latter case the formation of a double chloride cannot take place. For all those cases in which one of the chlorides used is decomposed by water, it is clear that this agent cannot be taken as a solvent. In other cases, and in fact in most cases, in which water is used, this must contain hydrochloric acid to prevent decomposition. In such cases it is probable that the hydrochloric acid unites with one of the chlorides to form a chlor-acid, just as water combines with some of the oxides to form the corresponding hydroxide or oxygen acid. It is well known that many metallic chlorides have the power to unite with hydrochloric acid, and that some of the compounds thus formed are to be regarded as the acids from which the double halides are derived. This is well shown by the compounds H_2PtCl_6 or $PtCl_4.2HCl$, $HAuCl_4$ or $AuCl_3.HCl$, H_2PbI_4 or $PbI_2.2HI$, and H_2HgI_4 or $HgI_2.2HI$.

Finally, the analogy between the double halides and the oxygen compounds of the same elements is shown by the fact that in both cases a compound of either an alkali metal or of one of the members of the calcium group is generally necessary to the formation of the more complex compound. In all cases in which a direct comparison of the formation of double halides with that of the formation of the oxygen salts of the same elements is possible, there is observed perfect analogy as regards the composition of the products.

4. *Acidic and Basic Halides.*

When a metallic hydroxide dissolves in and forms a compound with a strongly basic hydroxide, we speak of the former as having acid properties. Thus aluminium, chromium, and lead hydroxides are said to have acid properties. These properties are not, however, strongly marked, and in order that they may be stimulated to activity, contact with a strongly basic substance is necessary. The substances mentioned do not form salts with all bases, but only with the strongest ones. But facts of the same order are noticed in connection with the formation of the double halides. Aluminium chloride, for example, does not form double chlorides with all other chlorides, but only with those which are derived from elements with strongly marked basic properties, or with those which are derived from elements with strongly marked acidic properties. Similar facts are observed in the case of other chlorides, so that one is led to the conclusion that just as we have acidic and basic oxides, so too we have acidic and basic halides. In order that oxides may combine to form salts it is necessary in general that one should be acidic and the other basic. And in order further that halides may combine to form double halides, one must be acidic and the other basic, or there must be a certain oppositeness of chemical character which, as far as can be determined, is perfectly analogous to that which we have in mind when we speak of acid and basic properties.

This distinction between acidic and basic halides was first noticed by Von Bonsdorff,[1] and afterwards independently by Boullay.[2] In a letter to M. Gay Lussac, dated December 30, 1826, the former used these words: " En réfléchissant sur la grande analogie qui existe entre l'oxigène et quelques autres corps électro-négatifs par excellence, tels que le chlore, l'iode, etc., surtout par le phénomène du feu ou la combustion, qui a lieu quand ces élémens se combient à d'autres corps simples, et par la propriété que possèdent les mêmes élémens, dans nombre de cas, de gazéifier ces corps, il m'a paru très naturel, au moins très-probable, que les combinaisons de ces élémens avec les autres corps électro-négatifs, de même que les combinaisons de l'oxigène, donneraient naissance à des corps composés analogues aux acides, et que leurs combinaisons avec les corps simples électro-positifs produiraient des corps composés analogues aux bases salifiables."

After describing a number of new double salts he says: " Il se peut bien que je me sois trompé dans ma manière de voir la chose; cependant je hasarde de soumettre mon opinion, quelle qu'elle soit, au jugement des chimistes."

Boullay in the same year referred to this conception in the following words: "Je vais chercher à poser la question nettement et dans toute la simplicité qu'elle paraît avoir reelement. Lorsque l'oxygène se combine avec un autre corps, il en résulte généralement un composé doué d'une tendance acide ou basique. L'union de deux composés de ce genre doués de propriétés opposées donne naissance à des sels plus ou moins bien définis. L'idee de sel se rapporte donc toujours à l'union de deux corps composés eux-mêmes.—Sous ce point de vue, les chlorures, les iodures, les sulfures, ne sont point des sels et ressemblant théoriquement aux oxides d'une manière qui paraîtra tout-à-fait évidente à quiconque voudra bien examiner avec attention l'ensemble des travaux qui concernent ces corps. Ce rapprochement admis, les combinaisons de tous ces corps entre eux donnent naissance à diverses séries faciles à caractériser; mais dans l'application, les résultats sont restreints dans des limites souvent étroites par la nature même des corps mis en presence.—En effet, si d'un côté rien ne s'oppose à l'union des oxacides et des oxides, de l'autre aucune réaction particulière ne pourra troubler non plus l'union des sulfures entre eux, des chlorures entre eux, des iodures entre eux, et tous ces composés devront être classés ensemble comme de veritable sels."

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[1] Ann. chim. phys. **34**, 142 (1826).

[2] Ibid. **34**, 337 (1826).

Finally, at the close of his paper, Boullay draws this conclusion among others: "Que les iodures métalliques peuvent se partager en iodures acides, et en iodures basiques, et que l'union de ces corps donne naissance à de véritables sels."

Liebig[1] in 1827 commented upon the views of Von Bonsdorff unfavorably, although he says that the opinion of Von Bonsdorff differs but little from that of Berzelius regarding the double fluorides and the sulpho-salts.

Next, Berzelius, in his Jahresbericht[2] for the year 1829, took exception to the views of Von Bonsdorff and of Boullay. His objection is, however, as it appears, mainly one of definition. As sodium chloride is itself a salt, he holds that it cannot also be regarded as a base. The same reasoning would plainly keep us from ascribing acid properties to aluminium hydroxide because it is generally basic. At the time Berzelius wrote, chemists were accustomed to make a sharp distinction between acids and bases and salts, and the idea that one and the same substance could belong to two of these classes at the same time was not entertained. The great influence exerted by Berzelius and by Liebig prevented the general acceptance of the views put forward by Von Bonsdorff and by Boullay, and it seems that the close analogy which exists between double halides and oxygen salts has since then been almost completely lost sight of. My attention has been called by my friend, Dr. Wolcott Gibbs, to the fact that Dr. Hare of Philadelphia, half a century ago, held the same views as those which were put forward by Von Bonsdorff and Boullay. This is clearly shown by the following extracts from his Compendium, published in 1840: "The *chloro-salts* are generally obtained by mingling chlor-acids with chloro-bases, either in the wet or dry way. In the latter case, heat must be employed in order to facilitate their union. The *bromo-salts* and *iodo-salts* may in general be obtained in the same manner, by mingling brom-acids with bromo-bases, or iod-acids with iodo-bases" (p. 370). In another place (p. 359) he says: "Hence the nine following classes: *oxy-salts*, *sulpho-salts*, *seleni-salts*, *telluri-salts*, *chloro-salts*, *bromo-salts*, *iodo-salts*, *fluo-salts*, and *cyano-salts*. Obviously, of these the first four are formed by the *amphigen bodies*, and the rest by the *halogen bodies* of Berzelius."

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[1] Ann. chim. phys. **35**, 68 (1827).

[2] Vol. **8**, 138.

Further, in a paper published in Philadelphia in 1842, entitled "An Effort to refute the Arguments advanced in favor of the Existence in the Amphide Salts, of Radicals, consisting, like Cyanogen, of more than one Element," Dr. Hare discussed at some length the relations existing between the oxy-salts and the double halides.

It appears that Kane, Graham, and others took the ground with Berzelius that the halogen salts could not be regarded as acids and bases because they are salts. Dr. Hare saw clearly that the question was one of definition. He offered the following definition of salts, which he conceived "to be justified by the practice of modern chemists in general": "When two compounds, capable of combining with each other to form a tertium quid, have an ingredient common to both, and one of the compounds prefers the positive, the other the negative pole of the voltaic series, we must deem the former an acid, the latter a base."

At the present time there is no difficulty in recognising the close analogy between the halides and the oxides and sulphides. If we speak of sodium chloride as a salt, we do not hold that it is in any way fundamentally different from sodium oxide or sodium sulphide. Everything depends upon our definitions of acids and salts, and these definitions are unquestionably far from satisfactory. If we call sodium chloride a salt because it is derived from hydrochloric acid by the replacement of the hydrogen by sodium, we may with equal right call sodium hydroxide and sodium oxide salts, because they are derived from water by replacing part or all the hydrogen of the water by sodium. There is a difference in the ease with which the replacement can be accomplished in the two cases, but probably no one will maintain that the two acts differ fundamentally. Whatever we may call the compounds, then, it appears from a consideration of the facts discussed in the first part of this paper, that the action of halides upon halides is analogous to the action of oxides upon oxides, and that the compounds formed in the two cases are also analogous, not only in composition, but in their nature and structure. Whatever the power may be which makes it possible for two oxides of opposite chemical properties to act upon each other and form a neutral compound, it appears that this same power exists in halides.

The analogy between the formation of oxygen salts and double halides would appear more striking if we should regard the salts as formed by the action of an acidic oxide upon a basic oxide, or, in other words, if we should go back to the conception of this act which prevailed before the introduction of the so-called unitary system. That old conception is still as true as it ever was. The oxides can be divided into two classes with reference to their conduct towards one another. When an acidic oxide as, for example, sulphur trioxide, acts upon a basic oxide, as, for example, potassium oxide, a salt is formed according to the equation:

$$SO_3 + K_2O = K_2SO_4.$$

When, however, this same acidic oxide acts upon water, a substance which we call an acid is formed:

$$SO_3 + H_2O = H_2SO_4.$$

The two acts are of the same character, as is generally recognised. The formation of the acid or of the hydrogen salt is the first stage in the process of the formation of the salt. The formation of the other salts is effected by the replacement of the hydrogen of the so-called acid. The fundamental act in the formation of salts is, however, not this act of substitution, but the union of the water, which in this case acts as a basic oxide towards the acidic oxide. Going back then to this view in regard to the formation of oxygen salts, the analogy between this act and that of the formation of double chlorides will be clearly recognised.

But further, just as acidic oxides combine with water to form hydrogen salts or acids, so also some halides combine with halogen acids to form hydrogen salts or acids, which differ from the oxygen acids in containing a halogen in place of oxygen. The two acts are in all probability perfectly analogous, though the latter is much less common than the former. The following cases will suffice to illustrate this analogy:

$$SO_3 + H_2O = H_2SO_4$$
$$CO_2 + H_2O = H_2CO_3$$
$$PtCl_4 + 2HCl = H_2PtCl_6$$
$$SiF_4 + 2HF = H_2SiF_6$$
$$AuCl_3 + HCl = HAuCl_4$$
$$Cl_2O_3 + H_2O = 2HClO_2$$
$$B_2O_3 + H_2O = 2HBO_2.$$

Although the number of compounds of the kind here referred to thus far prepared is small, it is of importance to notice that in composition they are perfectly analogous to the so-called double salts formed by the combination of metallic chlorides, just as the oxygen acids formed by combination of water with acidic oxides are generally analogous in composition to the oxygen salts.

It appears from the above considerations that the halogen acids, or, to take one case, that hydrochloric acid, bears to double chlorides much the same relation that water bears to oxygen salts. We can easily conceive of a *chlorine system of chemistry* analogous to the *oxygen system*, which, owing to natural conditions, we are necessarily more familiar with. It is probable that, if we could use the compound hydrochloric acid as a solvent as we use the corresponding oxygen compound, water, we should be much more familiar with double chlorides than we now are. In our present system oxygen is the controlling element, and water is the most common reagent. Most double halides are decomposed by water, and, as we are generally forced to use water in making these compounds, it is clear that we start with unfavorable conditions for dealing with these salts. In the oxygen system water is the connecting link between acids and bases. We speak of it as neutral. Why? Because it does not act upon those compounds which we call acids, nor upon those which we call bases. Towards acidic oxides, however, it is unquestionably basic, and towards basic oxides like potassium, sodium and calcium oxides, it is unquestionably acid. In the chlorine system, hydrochloric acid bears a similar relation to the acidic chlorides on the one hand, and also towards the basic chlorides on the other. It is the connecting link between the acidic and the basic chlorides. These remarks apply with equal force to the other halogens.

A case of the same kind is presented by sulphur. As is well known, sulphides combine with one another in much the same way that oxides do, and form the sulpho-salts, which in composition are again perfectly analogous to the oxygen salts. Not many of these are known, but quite enough to show the analogy to the oxygen salts. The principal reason why not more are known appears to be, as in the case of the double halides, the fact that most of them cannot exist in the presence of water. In the sulphur system, hydrogen sulphide occupies the same position that water does in the oxygen system, and in order to work to the same advantage with the sulpho-salts we should have hydrogen sulphide available as a solvent. Probably no thinking chemist doubts that there is complete analogy between the sulpho-salts and the oxygen salts, and yet the evidence in favor of this view is, I think, by no means as strong as that upon which the view that the double halides are analogous to oxygen salts is founded.

4. *Theoretical.*

Thus far I have carefully abstained from putting forward any theory regarding the constitution of the double halides. But, if it is acknowledged that the evidence furnished by the facts is sufficient to show that the act involved in the formation of the double halides is of the same kind as that involved in the formation of oxygen salts, and that the products in the two cases are of the same general character, then the only explanation which suggests itself is this:

Two halogen atoms acting together can play the same part that the so-called linking oxygen atom plays in oxygen salts.

This view was first expressed by Naquet in his Principes de Chimie,[1] which appeared in 1867. On page 62 he gives this formula $\begin{matrix}\mathrm{Ag}\\ \mathrm{K}\end{matrix}\!>\!\mathrm{Cl}_2^{\mathrm{II}}$ to the compound formed by the union of potassium chloride and silver chloride. His explanation of the compound $HgI_2.2KI$, given on page 61, is much less satisfactory. In the same year Dr. Wolcott Gibbs[2] suggested that in the double halides perhaps two halogen atoms might play the part of one oxygen atom, and gave, by way of illustration, these formulas to acid potassium fluoride and potassium hydroxide:

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[1] Principes de Chimie fondée sur les Théories Modernes. Par A. Naquet. Paris, 1867.

[2] American Journal of Science (2 Series) **44**, 409 (1867).

$$\left.\begin{matrix}K^{III}F_2\\ H\end{matrix}\right\}\text{or } K^{III}(HF_2),$$

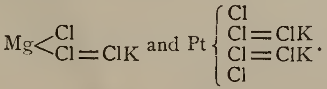
$$\text{and}\quad\left.\begin{matrix}K^{III}O^{II}\\ H\end{matrix}\right\}\text{or } K^{III}(HO).$$

It will be seen that at that time Dr. Gibbs held that potassium might act as a trivalent element, and he conceived the union between the hydrogen and the fluorine, and between the hydrogen and the oxygen, to be effected through this polyvalent potassium.

The fullest and clearest statement concerning the structure of the double halides is that of Blomstrand, published in his Chemie der Jetztzeit[1] in 1869. In my opinion, this book is not as much read as it deserves to be. There are many original views put forward in it, and chemical phenomena are throughout treated in a broad way, indicating clear insight. The discussion regarding the halogen double salts is well worthy of careful study. The author expresses himself concerning these compounds thus (p. 340):

"Die Haloiddoppelsalze entsprechen vollständig den eigentlichen Amphidsalzen, oder die in Doppelatomen wirkenden Haloide spielen durchaus dieselbe chemische Rolle, wie die wahren Amphide."

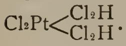
He conceives the halogen atoms to be trivalent, and explains the linking by formulas like the following:



$$Mg{<}\begin{matrix}Cl\\ Cl=ClK\end{matrix}\quad\text{and}\quad Pt\left\{\begin{matrix}Cl\\ Cl=ClK\\ Cl=ClK\\ Cl\end{matrix}\right..$$

The formulas given by Blomstrand differ somewhat in appearance from these, but they are evidently intended to express essentially the same conception.

In 1877 Jörgensen[2] made use of the same conception to explain chloroplatinic acid, which he expressed by the formula



$$Cl_2Pt{<}\begin{matrix}Cl_2H\\ Cl_2H\end{matrix}.$$

In 1881 Professor Mallet[3] advanced the same explanation for the double fluorides, after he had shown that at 30° the specific gravity of hydrofluoric acid gas corresponds to the formula H_2F_2. In his Kurzes Lehrbuch der Anorganischen Chemie, Kolbe suggests that possibly the double chlorides may be explained in the above way; and quite recently Francke,[1] in order to explain certain compounds of manganese obtained by him, has adopted the view that a double chlorine atom may take the place of an oxygen atom. In his Chemical Philosophy, Professor Cooke[2] suggests (p. 515) the possibility of such a double chlorine atom, not as an explanation of the double chlorides, but to account for the fact that crystallised stannic chloride, $SnCl_4.5H_2O$, retains two molecules of its water when heated. He thinks it possible that the salt which is left may have the formula

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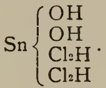
[1] Die Chemie der Jetztzeit vom Standpunkte der electrochemischen Auffassung aus Berzelius Lehre entwickelt. Von C. W. Blomstrand, Professor an der Universität zu Lund. Heidelberg, 1869.

[2] J. prakt. Chem. **16**, 352.

[3] This Journal **3**, 189 (1881).



$$Sn\begin{cases} OH \\ OH \\ Cl_2H \\ Cl_2H \end{cases}.$$

Professor Cooke evidently considers some of the double salts as molecular compounds, while he speaks of potassium chloroplatinate as a salt of the acid of the formula $H_2PtCl_6.6H_2O$, without giving an explanation of this formula.

In 1885 Armstrong[3] put forward the view that the double chlorides might be compounds of molecules held together by surplus affinity, and he gives the formula $Hg\genfrac{}{}{0pt}{}{Cl.ClK}{Cl.ClK}$ to the double chloride of mercury and potassium. Finally Heyes,[4] in discussing the subject of valency and validity, also suggested that the double halogen salts may be explained by assuming that the halogen atoms combine with each other.

From the above it is evident that the idea that two chlorine atoms can take the place of one oxygen atom in salts is not a new one, though it has certainly not been generally accepted. In accordance with this view, the constitution of some of the more common double halides may be represented by the following formulas, by the aid of which the analogy between these compounds and the oxygen compounds is clearly seen:

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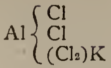
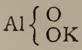
[1] Francke, J. prakt. Chem. [N. F.], **36**, 451 (1887).

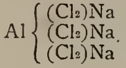
[2] Principles of Chemical Philosophy. By Josiah Parsons Cooke. Boston, 1881.

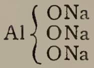
[3] British Assoc. Reports, 1885, 959.

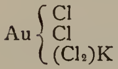
[4] Philosophical Magazine **25**, 221, 297.

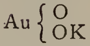

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{K}\end{array}\right.$$

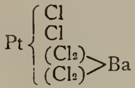

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OK}\end{array}\right.$$

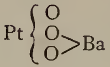

$$\mathrm{Al}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{Na}\\ (\mathrm{Cl_2})\mathrm{Na}\\ (\mathrm{Cl_2})\mathrm{Na}\end{array}\right.$$

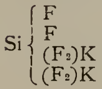

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{ONa}\\ \mathrm{ONa}\\ \mathrm{ONa}\end{array}\right.$$

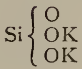

$$\mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{K}\end{array}\right.$$

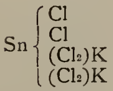

$$\mathrm{Au}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OK}\end{array}\right.$$

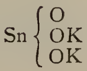

$$\mathrm{Pt}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ \left.\begin{array}{l}(\mathrm{Cl_2})\\ (\mathrm{Cl_2})\end{array}\right>\mathrm{Ba}\end{array}\right.$$

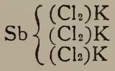

$$\mathrm{Pt}\left\{\begin{array}{l}\mathrm{O}\\ \left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Ba}\end{array}\right.$$

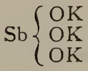

$$\mathrm{Si}\left\{\begin{array}{l}\mathrm{F}\\ \mathrm{F}\\ (\mathrm{F_2})\mathrm{K}\\ (\mathrm{F_2})\mathrm{K}\end{array}\right.$$

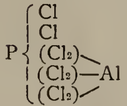

$$\mathrm{Si}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OK}\\ \mathrm{OK}\end{array}\right.$$

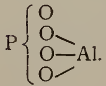

$$\mathrm{Sn}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{K}\\ (\mathrm{Cl_2})\mathrm{K}\end{array}\right.$$


$$\mathrm{Sn}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OK}\\ \mathrm{OK}\end{array}\right.$$


$$\mathrm{Sb}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{K}\\ (\mathrm{Cl_2})\mathrm{K}\\ (\mathrm{Cl_2})\mathrm{K}\end{array}\right.$$


$$\mathrm{Sb}\left\{\begin{array}{l}\mathrm{OK}\\ \mathrm{OK}\\ \mathrm{OK}\end{array}\right.$$


$$\mathrm{P}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ \left.\begin{array}{l}(\mathrm{Cl_2})\\ (\mathrm{Cl_2})\\ (\mathrm{Cl_2})\end{array}\right\rangle\!-\mathrm{Al}\end{array}\right.$$


$$\mathrm{P}\left\{\begin{array}{l}\mathrm{O}\\ \left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{array}\right\rangle\!-\mathrm{Al.}\end{array}\right.$$

As will be seen, all that is required is that we assume the power of a halogen atom to unite with itself to form a bivalent group, and we have a satisfactory theory to account for the large class of compounds with which we are dealing. As I have already said, there are some compounds included in the class which do not correspond in composition to any one of the fundamental forms. These can, however, be easily explained, just as we explain the salts of the poly-acids. Thus we have not only the cases given on p. 298, viz:

$2\mathrm{AuCl_3.KCl}$ or $\mathrm{KAu_2Cl_7}$
$2\mathrm{AuCl_3.MgCl_2}$ or $\mathrm{MgAu_2Cl_8}$
$3\mathrm{BiCl_3.2KCl_2}$ or $\mathrm{K_2Bi_3Cl_{11}}$,

but more complex ones, of which those represented by the following formulas are fair examples:

$2ZnI_2.KI$ or KZn_2I_5
$2ZnI_2.BaI_2$ or $BaZn_2I_6$
$2HgCl_2.RbCl$ or $RbHg_2Cl_5$
$4TaF_2.3KF$ or $K_3Ta_4F_{11}$
$2SbI_3.3KI$ or $K_3Sb_3I_9$
$2SbI_3.3NaI$ or $Na_3Sb_3I_9$
$3AlF_3.5NaF$ or $Na_5Al_3F_{14}$
$2ClF_4.3KF$ or $K_3Cl_2F_{11}$.

The salt KAu_2Cl_7 is evidently derived from an acid HAu_2Cl_7. The more common form of chlorauric acid is $HAuCl_4$. The relation between the two is expressed by the equation:

$$2HAuCl_4 = HAu_2Cl_7 + HCl;$$

or perhaps better by the formulas:

$$\mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right. \qquad\qquad \begin{array}{l}\mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.\\ \quad\;\;(\mathrm{Cl_2})\\ \mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right.\end{array}.$$

The salt $MgAu_2Cl_8$ is derived from the acid $H_2Au_2Cl_8$. This is related to the fundamental acid, as shown thus:

$$\mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right. \qquad\qquad \begin{array}{l}\mathrm{Au}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{H}\\ \mathrm{Cl}\end{array}\right.\\ \quad\;\;(\mathrm{Cl_2})\ \text{or}\\ \mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right.\end{array} \quad \begin{array}{l}\mathrm{Au}\left\{\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.\\ \quad\;\;(\mathrm{Cl_2})\\ \mathrm{Au}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{H}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right.\end{array}.$$

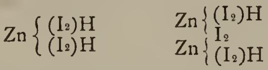
The salt $K_2Bi_3Cl_{11}$ is derived from the acid $H_2Bi_3Cl_{11}$, and this is related to the fundamental form H_3BiCl_6 as shown below:

$$3H_3BiCl_6 = H_2Bi_3Cl_{11} + 7HCl;$$

$$\mathrm{Bi}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{H}\\ (\mathrm{Cl_2})\mathrm{H}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right. \qquad\qquad \begin{array}{l}\mathrm{Bi}\left\{\begin{array}{l}(\mathrm{Cl_2})\mathrm{H}\\ \mathrm{Cl}\end{array}\right.\\ \quad\;\;(\mathrm{Cl_2})\\ \mathrm{Bi}\left\{\begin{array}{l}\mathrm{Cl}\end{array}\right.\\ \quad\;\;(\mathrm{Cl_2})\\ \mathrm{Bi}\left\{\begin{array}{l}\mathrm{Cl}\\ (\mathrm{Cl_2})\mathrm{H}\end{array}\right.\end{array}$$

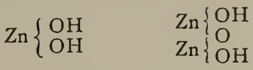
One more example will suffice. The salt $BaZn_2I_6$ is derived from the acid $H_2Zn_2I_6$, and this is related to the fundamental form H_2ZnI_4 as shown below:

$$2H_2ZnI_4 = H_2Zn_2I_6 + 2HI;$$



$$\mathrm{Zn}\left\{\begin{matrix}(I_2)H\\(I_2)H\end{matrix}\right. \qquad \begin{matrix}\mathrm{Zn}\left\{\begin{matrix}(I_2)H\\ I_2\end{matrix}\right.\\ \mathrm{Zn}\left\{(I_2)H\right.\end{matrix}$$

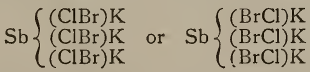
The analogy between these relations and those which exist between the corresponding oxygen compounds will appear without explanation, though one case may be given. For the purpose of direct comparison the last case cited serves very well. We can easily conceive of the existence of a hydroxide of zinc of the formula $H_2Zn_2O_3$ derived from the normal hydroxide $Zn(OH)_2$. These relations are expressed thus:



$$\mathrm{Zn}\left\{\begin{matrix}OH\\OH\end{matrix}\right. \qquad \begin{matrix}\mathrm{Zn}\left\{\begin{matrix}OH\\ O\end{matrix}\right.\\ \mathrm{Zn}\left\{OH\right.\end{matrix}$$

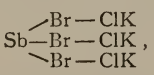
Plainly this compound $H_2Zn_2O_3$ is analogous to the iodine compound $H_2Zn_2I_6$. All the other complicated cases can be explained as readily as those cited.

In the mixed double halides it is necessary to assume that two halogen atoms of different kinds acting together play the part of the double chlorine atom in the double chlorides, and of the oxygen atom in the oxygen salts. The structure of the compound formed by the union of antimony trichloride and potassium bromide, for example, should be represented thus:



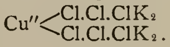
$$\mathrm{Sb}\left\{\begin{matrix}(ClBr)K\\(ClBr)K\\(ClBr)K\end{matrix}\right. \quad \text{or} \quad \mathrm{Sb}\left\{\begin{matrix}(BrCl)K\\(BrCl)K\\(BrCl)K\end{matrix}\right.$$

It is probable that the linking group would adjust itself in accordance with the affinities, and if, as is assumed in the valence hypothesis, a definite arrangement of the atoms with reference to one another exists in the molecule, the more probable view is that the structure should be represented by the following formula:



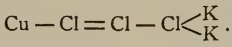
for the reason that the specific affinity of chlorine for potassium is greater than that of bromine for antimony. This would explain why it is that the same salt is formed by union of antimony trichloride and potassium bromide that is formed by union of antimony tribromide and potassium chloride, a fact which was brought to light by R. W. Atkinson[1] working in Williamson's laboratory. The explanation is not a forced one, for, as is well known, the halogens exchange places with the greatest ease when their metallic salts are brought together.

With regard to the salt which differs in its composition from all the other double halides, viz. that of the formula $CuCl.2KCl$, attention has already been called to the fact that it is derived from the unsaturated compound $CuCl$. Whether this has anything to do with its anomalous composition can only be determined by further investigation, and work bearing upon this point has already been begun in this laboratory. Blomstrand does not hesitate to assume that a triple chlorine atom can play a part somewhat like that played by the double chlorine atom, and according to this he represents the compound of cuprous chloride and potassium chloride by this formula:



$$\mathrm{Cu''}{<}\begin{array}{l}\mathrm{Cl.Cl.ClK_2}\\ \mathrm{Cl.Cl.ClK_2}\end{array}.$$

In terms of the valence hypothesis this view is expressed thus:



$$\mathrm{Cu-Cl=Cl-Cl}{<}\begin{array}{l}\mathrm{K}\\ \mathrm{K}\end{array}.$$

Whatever the correct explanation of this compound may be, it is clear from the facts that the condition existing in it is an unusual one. The above formula appears to me to be highly speculative, and before offering any other or making any further effort to explain the compound, it seems to me better to wait until we have more facts at disposal. Before leaving this part of the subject, however, I will again call attention to the fact that this is the only well-authenticated exception to the simple conception of double halides in a list of nearly four hundred compounds.

The question as to whether the chlorine in these compounds is to be regarded as bivalent or trivalent is one which will be asked. Blomstrand, as we have seen, regards it as trivalent. I cannot see that at present we have any evidence which justifies us in the use of the expression $-Cl=Cl-$ rather than $-Cl-Cl-$. It is possible that as investigation proceeds, light may be thrown upon this part of the subject. Perhaps the study of such compounds as that of the formula $CuCl.2KCl$ may be of service in this direction. At present all that we can fairly say is that *the double halogen atom acts like the linking oxygen atom, and is therefore bivalent.*

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[1] J. Chem. Soc. **43**, 289 (1883).

5. *Objections to the Theory.*

What objection can be offered to the theory of double halides discussed in the preceding pages? The one which undoubtedly has, and perhaps will have, the most weight with the great majority of chemists is that it is not in accordance with the prevailing views regarding the valence of the halogens. Horstmann in his Theoretische Chemie[1] (p. 340) says in regard to this subject: "Die Halogendoppelsalze sind fast so zahlreich als die Sauerstoffsalze und haben mit denselben sehr häufig unverkennbare Analogien, die man früher mehr beachtete als heute." After giving some examples, he says further: "Berücksichtigt man, dass der chemische Charakter mancher Elemente den Halogenen gegenüber sich wohl etwas anders äussern kann, als dem Sauerstoff gegenüber, so erkennt man in dem vorstehenden Beispiele den vollkommenen Parallelismus mit den Sauerstoffsalzen, welche die zeitweilig übliche Bezeichnung jener Doppelverbindungen als Chlorosalze (Bromosalze, etc.) rechtfertigt. Als weitere Abtheilung der Salze würden noch die Schwefeldoppelverbindungen oder Sulfosalze hinzukommen.— Nach dualistischer Ansicht, mit Benutzung der alten Aequivalentgewichte, konnte allen diesen Verbindungen analoge Constitution zuerkannt werden. Aber die Valenzlehre hat die Analogie gestört. Nur die Verbindungen des zweiwerthigen Sauerstoffs und Schwefels konnten durch Atomverkettung erklärt werden. Die Chlorosalze und die entsprechenden Salze der anderen Halogenen blieben als dualistisch zusammengesetzte Molecularverbindungen zurück.—Nun würde der atomistische Zusammenhalt aller solchen Halogenverbindungen erklärlich sein, wenn man sich darin die Halogene mehrwerthig wirkend vorstellen dürfte. Allein die früher angeführten Gründe sprechen für die Mehrwerthigkeit der Halogene nur in ihren Verbindungen mit dem negativen Sauerstoff, nicht mit den positiven Metallen. Jene Erklärung ist daher nicht sehr wahrscheinlich. Sie könnte höchstens für einige Doppelverbindungen des Fluors, z. B.

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[1] Lehrbuch der Physikalischen und Theoretischen Chemie. Von A. Horstmann und H. Landolt. Zweite Abtheilung. Theoretische Chemie einschliesslich der Thermochemie. Von A. Horstmann. Braunschweig, 1885. (This is a part of the first volume of the last edition of Graham-Otto's Ausführliches Lehrbuch der Chemie.)

$HNaF_2$, gerechtfertigt scheinen, weil die Dampfdichte der Fluorwasserstoffsäure selbst bei niedriger Temperatur auf die Molecularformel H_2F_2 und auf die Zweiwerthigkeit des Fluors hinweist."

Horstmann then goes on to say that another explanation is on the whole more desirable, or at least that it appears to be capable of wider application (scheint allgemeiner anwendbar zu sein). The other explanation is this, that the formation of double halides is due to the stimulating effect of the alkali salt of the halogen upon the other halide. Just as we commonly explain the union of ammonia with hydrochloric acid by assuming that under the influence of the hydrogen and chlorine the nitrogen of the ammonia becomes quinquivalent, so he thinks it probable that, when potassium chloride acts upon platinic chloride, the platinum becomes octovalent. Such compounds as $SbCl_3.KBr$, $SbCl_3.2KCl$, and $SbCl_3.3KCl$, would, according to this, necessitate the assumption that antimony can act with a valence of five, of seven, and of nine! Similar results are reached in an attempt to apply this hypothesis to the compounds of aluminium and of chromium. Horstmann's objection to the view that the halogens may be polyvalent in the double halides is that the study of other compounds leads to the conclusion that the halogens exhibit polyvalence only towards oxygen. So also it might with equal force be objected to the explanation which he accepts, that the study of other compounds of antimony and of aluminium does not justify the assumption that they can act with a valence of nine. The question is, *what conclusion does the study of the double halides themselves lead to?* I hold that this study leads unmistakably to the conclusion that in them the halogen atoms, or some of these atoms, are polyvalent. We do not now hesitate to accept the conclusion that the halogens are polyvalent towards oxygen, whereas a few years ago this idea met with but little favor. We cannot further, as it seems to me, avoid the conclusion that the halogens are polyvalent towards one another. How else can we rationally explain the compounds ICl_3 and IF_5? But, if the halogens can combine directly with each other and form comparatively stable compounds, it is not surprising that when they are in combination with metallic elements the compounds which they form should be more stable. It appears to me, however, that the strongest argument in favor of the polyvalence of the halogen atoms in the double halides is to be found in the unmistakable analogy between these compounds and the oxygen salts which was discussed so fully in the early part of this paper. Horstmann clearly recognises this analogy. He speaks of the perfect parallelism which exists between the two classes of compounds. When it comes to the explanation he is willing to lose sight of this analogy and take refuge in an hypothesis which can fairly be said to be much less probable than the one which he discards. The analogy between the double halides and the oxygen salts is perfectly clear to him, yet he says, "Aber die Valenzlehre hat die Analogie gestört." I should rather say that the valence hypothesis in its old rigid form has prevented chemists from recognising the analogy, and has prevented them from using analogous expressions for analogous compounds; and I cannot help feeling that, on a reconsideration of the facts, so fair-minded a man and so clear a thinker as Professor Horstmann will agree with me on this point. To which should we give the greater weight, to one phase of the imperfectly developed and ever-changing valence hypothesis, or to a large number of well established facts? Can any one be in doubt?

I have given special attention to the views of Horstmann because they are put forward by a man of recognised pre-eminence and in a book which deservedly has great influence; and, further, because I believe that his presentation of the case is as strong as it can be made from the point of view of those who are under the subjection of the valence hypothesis. I suppose that the majority of chemists think as Professor Horstmann does, or at least they accept the same conclusion without thinking. I have been surprised to find that that cautious writer and philosopher, Professor Lothar Meyer, is not willing to adopt the view that the halogens are polyvalent in the double halides, but that he is inclined to accept an explanation like that accepted by Horstmann. He remarks on this subject: "Der Annahme aller dieser Formeln steht aber das eine schwere Bedenken gegenüber, dass man in ihnen Fluor und Chlor auch dem positiven Wasserstoffe und den Metallen gegenüber mehrwerthig annehmen muss, wozu sonst keine Nöthigung vorliegt."[1] To this argument the same reply is justified as that already made to the similar argument of Horstmann. The question is, what conclusion does the study of the double halides themselves lead to?

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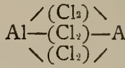
[1] Die Modernen Theorien der Chemie und ihre Bedeutung für die chemische Mechanik von Dr. Lothar Meyer, 5te Auflage, 1884.

6. *Applications.*

If it be true that chlorides can combine with other chlorides through the chlorine atoms, as I think has been shown, it is quite possible that this linking power of halogens may make itself felt in other similar cases. Thus it seems to me probable that aluminium chloride, instead of existing under ordinary circumstances as the simple molecule $AlCl_3$, is itself a compound analogous to the double halides, having the formula  $\mathrm{Al}\begin{array}{c}\diagup(\mathrm{Cl}_2)\diagdown\\ -(\mathrm{Cl}_2)-\\ \diagdown(\mathrm{Cl}_2)\diagup\end{array}\mathrm{Al}$.[1] If this is the constitution of aluminium chloride, we can quite understand why such peculiar results should be obtained in the determination of the specific gravity of this compound. These results show clearly that at temperatures just above the boiling point, the specific gravity is in accordance with a more complex formula. It is probable that the molecules at the lower temperature have the formula Al_2Cl_6, and that when the temperature is raised these break down gradually to the simpler form $AlCl_3$. The formation of an ordinary double chloride from aluminium chloride is not, according to this view, a simple addition, but it involves a preliminary breaking down, as represented in this equation:

$$Al_2Cl_6 + 2KCl = 2KAlCl_4.$$

The above view, further, would explain why the compounds of aluminium with organic radicals correspond to the simpler formulas, as, for example, $Al(CH_3)_3$, $Al(C_2H_5)_3$, as shown to be the case by the recent work of Quincke.[2] Of course, if the above arguments are of value with reference to the case of aluminium chloride, a similar explanation appears probable in the case of other metallic chlorides.

Another thought suggests itself. No satisfactory explanation has yet been offered for the reaction of Friedel and Crafts for the synthesis of hydrocarbons. It is, however, generally conceded that the aluminium chloride used in the reaction forms an unstable compound with the halogen derivative. The formation of such compounds is easily understood if we concede to chlorine the linking power. Just as aluminium chloride and potassium chloride combine to form the stable potassium chloraluminate, so we can easily conceive that ethyl chloride and aluminium chloride may combine to form the unstable compound, ethyl chloraluminate, $C_2H_5AlCl_4$. In this compound, further, a part of the chlorine would probably be held much less firmly, and be better able to enter into reaction than the chlorine of either ethyl chloride or of aluminium chloride taken separately. Or it may be that in some cases a compound of the halogen derivative with aluminium chloride is not formed, but that the disturbing influence of the aluminium chloride is felt in its attraction for the chlorine of the halogen derivative, so that the latter is less stable and more susceptible to reagents than when the aluminium chloride is not present. Granted the linking power of chlorine, and the action of aluminium chloride in the Friedel and Crafts reaction is, it appears to me, no longer mysterious.

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[1] See also Heyes, Philosophical Magazine **25**, 307.

[2] Ber. d. chem. Gesell. **22**, 551 (1889).

7. *Nomenclature.*

The acceptance of the views above set forth concerning the nature and constitution of the double halides will necessarily lead to a revision of the nomenclature of these compounds in harmony with that proposed by Von Bonsdorff, Boullay, and Hare. In some cases chemists have adopted the better names without at the same time adopting the conception of the compounds upon which the names are founded. Thus it has become more and more customary to speak of fluosilicates and of chloroplatinates, but in most cases the older names, such as double chloride of magnesium and potassium, double chloride of chromium and sodium, are still used. The change required by the acceptance of the view that the double chlorides are chloro-salts is simple and will suggest itself. Just as the salts formed with platinic chloride are called *chloroplatinates*, so those with aluminic chloride should be called *chloraluminates;* those with magnesium chloride, *chloromagnesates;* those with zinc chloride, *chlorozincates;* those with auric chloride, *chloraurates*, etc., etc. So, also, the acids from which these salts are derived should be named as *chloroplatinic* acid is named. We should speak of *chlorauric acid*, of *iodoplumbous acid*, of *iodohydrargyric acid*, etc., etc. That some of these names lack elegance can scarcely be urged as a serious objection to their use. It may safely be said that they are more elegant, as in every other respect more satisfactory, than those at present in use.

8. *Summary and Conclusion.*

In the foregoing I have called attention:

(1) To the large number of the substances known as double halides.

(2) To the simplicity of the law governing the composition of these compounds.

(3) To the analogy of these compounds with the oxy-salts.

(4) To the arguments which lead to the conclusion that there are in general two classes of halides, which we may regard as basic and acidic, and which bear to each other the same relations that basic oxides bear to acidic oxides.

(5) To the arguments which, as it appears to me, fully justify the conclusion that in the double halides we have a double halogen atom playing the same rôle that the linking oxygen plays in oxy-salts.

Further, let me again say that the views expressed in this paper have in past years, in one form or another and in a more or less comprehensive way, been advocated by others. My object is to direct the attention of chemists to the character of the evidence which is available, as I believe that an unprejudiced study of this evidence will lead to the acceptance of the views put forward, and I feel sure that this will contribute to a more rational treatment of a large class of chemical compounds, and to a clearer conception of a large class of chemical phenomena.

I propose in the future to devote a part of my time to experimental work bearing upon the double halides, and two investigations in this field have already been begun in this laboratory. Some of the work done in former years evidently needs revision, and at first attention will be directed chiefly to such revision. There are, however, several lines which may, I think, be followed with profit, though, as we have already found, the work involves serious experimental difficulties.

As regards the work thus far begun, I may say that Mr. G. M. Richardson is at present investigating some of the compounds obtained from stannous chloride, with the main object of determining whether this unsaturated compound is capable of yielding other chloro-salts besides those of the general formula M_2SnF_4; and Mr. C. H. Herty has been engaged for some time in the study of the iodoplumbates, which were first studied by Boullay in 1826.[1] Some interesting results have been obtained in the course of this investigation. In anticipation of the publication of the complete results, it may be stated now with confidence that a salt of the composition $PbI_2.4KI$ or K_4PbI_6, as described by Boullay, cannot be made by the method described in his paper; and that the one salt formed with most ease when lead iodide and potassium iodide are brought together under a great variety of circumstances, has the composition $KPbI_3 + H_2O$ or $PbI_2.KI + H_2O$. The chloroplumbates and bromoplumbates as well as the mixed double halides of lead, if they can be obtained, will also be made the subject of study. Many other subjects for work in this field suggest themselves, and it is hoped that some of these at least can be taken up in the immediate future.

JOHNS HOPKINS UNIVERSITY, CHEMICAL LABORATORY, *May*, 1889.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

III.—ON THE CONDUCT TOWARDS ALCOHOL OF THE DIAZO COMPOUNDS OBTAINED FROM THE THREE NITRANILINES, AND OF THOSE OBTAINED FROM THE THREE AMIDO-BENZOIC ACIDS.

BY IRA REMSEN AND R. O. GRAHAM.

In an earlier investigation,[2] Orndorff and one of us have shown that when the salts of diazo-benzene are decomposed in alcohol, phenetol is the main product, but little benzene being formed; and, further, that the salts of ortho- and meta-diazo-toluene conduct themselves differently from those of the isomeric para-compound. About 50 per cent. of ortho-diazo-toluene sulphate is converted by alcohol into the ethyl ether of ortho-cresol; and about 40 per cent. of the meta-compound undergoes the same transformation; while, when para-diazo-toluene sulphate is decomposed in alcohol, about 45 per cent. is converted into toluene, and 18 per cent. into the ethyl ether of para-cresol. As it was thus shown that the presence of the methyl group exerts an influence on the course of the reaction, it became desirable to investigate other cases, in order, if possible, to discover whether other groups also exert an influence, and whether this is the same as that exerted by methyl. The first case examined was that of the three diazo-compounds obtained from the nitranilines. Then we took up the three diazo-compounds formed from the amido-benzoic acids.

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[1] Ann. chim. phys. [2 Série] **34** (1827).

[2] See this Journal **9**, 387.

EXPERIMENTS WITH THE NITRO-DIAZO-BENZENES.

Preparation of ortho-nitraniline.—Ortho-nitraniline was prepared according to the method described by Körner,[1] by treating acetanilide with nitric acid of specific gravity 1.465. Körner advises that the acid employed be free from the lower oxides of nitrogen. But an acid of the above specific gravity, which was prepared by mixing ordinary concentrated and fuming nitric acids, was found to be more satisfactory than the acid when free of the lower oxides. The treatment with nitric acid was conducted as described below. Several small beakers were placed in shallow pans filled with powdered ice. Into each of these, twenty grams of the acid were poured, and then 10 grams powdered acetanilide thrown upon the acid. After a few moments, a violent reaction took place; and when this was over, the contents of the beaker were thrown into a large evaporating dish containing lumps of ice. After all the acetanilide had been converted into the nitro-compound, the latter was filtered from the ice-water, and then thrown into an excess of a strong solution of potassium hydroxide. A mixture of para- and ortho-nitranilines was thus obtained. By distilling in steam for several days, the volatile ortho-nitraniline was carried over with the water-vapor. About 1200 grams of acetanilide yielded 115 grams of ortho-nitraniline. By heating the non-volatile portion with very dilute alcohol, filtering, and boiling with bone-black, the para-nitraniline was obtained pure.

Preparation of ortho-diazo-benzene nitrate.—This salt was prepared as follows: 10 grams ortho-nitraniline were treated in a flask with 45 cc. dilute and a little concentrated nitric acid. The flask containing the solution of the nitrate thus formed was placed in ice-water, and a rapid current of nitrogen trioxide passed through the liquid, until completion of the reaction was indicated by the free escape of nitrogen trioxide. The contents of the flask were filtered and the filtrate placed in a freezing mixture. The thoroughly cooled liquid was treated with 200 cc. cold anhydrous ether, the two being thoroughly shaken together. Then 75 cc. cold alcohol were added, and the mixture thoroughly shaken in the freezing mixture. Under these circumstances the diazo-compound crystallised out. It was quickly filtered, washed with ether, and then spread upon filtering paper. 10 grams ortho-nitraniline yielded 9 grams ortho-nitro-diazo-benzene nitrate. In one attempt to precipitate the diazo-compound by placing the liquid containing it in a freezing mixture and adding alcohol, an active decomposition began at once, and this ended in a violent explosion.

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[1] Jahresbericht für Chemie, 1875, 344.

Ortho-nitro-diazo-benzene nitrate forms small tabular crystals which at first are pure white, but they change almost immediately to golden yellow. The compound explodes when heated, but not by concussion. It is easily soluble in water.

Ortho-nitro-diazo-benzene sulphate was made in the same way as the nitrate. 10 grams ortho-nitraniline yielded 11 grams of the sulphate. The salt, which is colorless and very stable, crystallises in small plates. It is not decomposed by concussion; and when heated it explodes feebly. If a free flame is brought in contact with it, it puffs up and becomes charred.

Decomposition of ortho-nitro-diazo-benzene sulphate by alcohol.—The dried salt was brought into a dry flask with absolute alcohol, and, after the flask was connected with an inverted condenser, gently heated on the water-bath. Decomposition began when the temperature of the water-bath reached 70°, and it then proceeded quietly to the end. A strong odor of aldehyde was noticed. The reaction was a very clean one. On distilling in steam, nitrobenzene passed over, and in the flask a small quantity of a brown semi-crystalline solid remained, but this could not be purified by crystallisation. 22 grams of the sulphate yielded 9 grams nitrobenzene, a yield which amounts to 54 per cent. of the theoretical.

Attempts were made to obtain the products of the decomposition of the sulphate by water and in toluene, but in the former case only a tar was formed, and from this no definite product could be isolated; while on heating with toluene, even at the boiling point of the hydrocarbon, no action took place for some time, when suddenly the entire quantity decomposed at once, causing vigorous explosion, but only a tarry mass was left behind.

Preparation of meta-nitro-diazo-benzene nitrate.—10 grams meta-nitraniline were thoroughly mixed with 15 cc. strong, and a little dilute, nitric acid, and the nitrate thus formed. This was suspended in 100 cc. absolute alcohol in a flask surrounded by ice-water, and a rapid current of the oxides of nitrogen passed through the liquid for an hour. The diazo-compound was precipitated out as fast as it was formed. At the end of the operation a little ether was added, and the liquid placed in a freezing mixture for the purpose of completing the precipitation of the diazo-compound. The compound was filtered with the aid of the pump, washed with absolute alcohol and with ether, and afterwards thoroughly dried by exposing it to the air on filter paper. 10 grams of meta-nitraniline gave 12 grams of the nitrate of the diazo-compound.

Meta-nitro-diazo-benzene nitrate crystallises in small grains, which at first are almost white, but soon become brown when exposed to the air. It is very soluble in water. It changes but slightly, even when exposed to the air for twenty-four hours. It explodes by concussion, though not violently.

Preparation of meta-nitro-diazo-benzene sulphate.—The sulphate was made as follows: 10 grams meta-nitraniline were placed in a flask, and a slight excess of concentrated sulphuric acid added, and a few cubic centimeters of water. After stirring for some time until the change to the white sulphate was complete, 100 cc. of ordinary alcohol were added, and the oxides of nitrogen passed into the liquid until they were no longer absorbed. The liquid contents of the flask were then quickly poured upon a filter. The filtrate was cooled by means of a freezing mixture, and ether added, when the diazo-compound was soon thrown down as a granular powder. 10 grams meta-nitraniline yielded 11.5 grams of the sulphate.

Meta-nitro-diazo-benzene sulphate appears in perfectly white granular crystals. It is readily soluble in water, and is quite stable. When allowed to stand for some time in a desiccator over sulphuric acid, it became colored a delicate pink; but even after standing for several days, there appeared to be no material decomposition. It is not decomposed by concussion. When heated by a free flame, it deflagrates and swells up, leaving a black residue.

Decomposition of meta-nitro-diazo-benzene nitrate by alcohol.—This was treated in the same way as the sulphate of ortho-nitro-diazo-benzene. When the temperature of the water-bath reached 70°, the decomposition began, and it was completed at 75°. Aldehyde was given off freely, and a reddish liquid resulted. After the action was over, the excess of alcohol was distilled off, water added, and the contents of the flask distilled in steam. The only product of decomposition which could be isolated was the nitro-benzene, which passed over with the water-vapor. A tarry residue remained in the flask. From 46 grams of the nitrate 15 grams nitro-benzene were obtained, the yield being 55 per cent. of the theoretical.

Decomposition of meta-nitro-diazo-benzene sulphate by alcohol.—Decomposition began at 65° and was completed at 70°. Aldehyde was given off freely. Nitro-benzene was carried over with steam, and no other product was isolated. 22 grams of the sulphate yielded 7 grams nitro-benzene, a yield of about 66 per cent.

The decomposition of the nitrate and of the sulphate by water and in toluene was studied, but definite products could not be obtained.

Preparation of para-nitro-diazo-benzene nitrate.—In consequence of the ease with which the diazo-amido-compound is formed when para-nitraniline nitrate is treated with nitrous acid, considerable difficulty was experienced in preparing the diazo-compound. By working as described below, the compound is easily obtained. 20 grams para-nitraniline were placed in a flask with 60 cc. dilute nitric acid. On gently heating, the nitrate was formed. The contents of the flask were then cooled by ice, and treated with a rapid current of the oxides of nitrogen. Whenever a precipitate of the diazo-amido-compound began to form, the flask was removed for an instant from the ice-water. In the course of twenty-five minutes the end of the reaction was reached, and this was shown by a change of color of the solution to a dingy green, and by the escape of oxides of nitrogen. After cooling in a freezing mixture of ice and hydrochloric acid, the liquid was quickly filtered by the aid of the pump. To the thoroughly cooled liquid about 250 cc. absolute alcohol and 150 cc. anhydrous ether were added, and the flask constantly shaken in the freezing mixture. In a few minutes the needle-shaped crystals of the diazo-compound separated out. These were quickly filtered and washed on the filter, first with absolute alcohol, then with anhydrous ether, and spread out on filter paper. 20 grams of para-nitraniline gave 16 grams of the nitrate.

Para-nitro-diazo-benzene nitrate forms long needle-like crystals of a beautiful silky lustre. When first formed it is white, but it soon becomes yellow by exposure to the air. It explodes violently when heated or struck. It is readily soluble in water, and almost insoluble in alcohol and in ether.

Decomposition of para-nitro-diazo-benzene nitrate by alcohol.— This compound was treated with alcohol in the same way as the ortho- and the meta-compounds. The decomposition began at 70° and was rapidly completed at 75°. After the decomposition was finished, the alcohol was distilled off and the residue distilled with water-vapor. The only product isolated was nitro-benzene, which was recognised by its odor, specific gravity, and boiling point. From 40 grams of the diazo-compound 16 grams nitro-benzene were obtained, a quantity which represents a yield of 70 per cent.

Experiments on the conduct of para-nitro-diazo-benzene nitrate when treated with water and with toluene gave unsatisfactory results. Definite products could not be obtained.

The above experiments are of interest as showing that the presence of the nitro-group in any one of the three possible positions relatively to the diazo-group causes the reaction with alcohol to take place in a different way from that in which it takes place when the nitro-group is not present. At the same time it will be observed that the influence exerted by this group is different from that exerted by the methyl-group.

EXPERIMENTS WITH THE DIAZO-BENZOIC ACIDS.

Decomposition of ortho-diazo-benzoic acid nitrate by alcohol.— The nitrate was made by the method described by Griess.[1] From 10 grams of ortho-amido-benzoic acid 12 grams of the nitrate of the diazo-compound were obtained. On heating the nitrate with absolute alcohol on the water-bath, decomposition began at 60° and was completed at 70°. The alcohol was distilled off, the residue diluted with water and distilled in steam. An oil which was heavier than water passed over. The oil was separated from the water and dried over calcium chloride, when it was found to boil at 213°. This fact, taken together with the characteristic odor of the oil, showed it to be ethyl benzoate. Further, when boiled with potassium hydroxide it was saponified, yielding benzoic acid with all its characteristic properties. A small quantity of benzoic acid was obtained from the contents of the flask from which the ethyl benzoate had been expelled by steam, but the ethyl benzoate was formed in by far the larger quantity. Of the latter, 8 grams were obtained from 24 grams of the diazo-compound in the form of nitrate, a yield of 53 per cent. of the theoretical.

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[1] Ber. d. deutsch. Ges. **9**, 1653.

Decomposition of ortho-diazo-benzoic acid nitrate in toluene.—8 grams of the nitrate were heated in toluene on a water-bath. No signs of decomposition were noticed until the boiling point of water was reached; and at this point the action set up was so violent as to necessitate removal from the bath; and for some time after the removal it continued vigorously. Meantime the flask was constantly shaken, and, when the action ceased, it was again heated until the decomposition was finished. Barium carbonate in suspension was then added and the whole thoroughly shaken. The toluene was separated and tested for substances in solution, but nothing was found. The water solution was boiled to free it from all toluene, and then filtered. After acidifying, a precipitate was formed which, after being repeatedly boiled with bone-black and recrystallised, appeared in the form of long, yellowish, needle-shaped crystals which melted at 228°. The solution of this acid gave a blood-red precipitate with ferric chloride. These are the properties ascribed by Griess[1] to unsymmetrical nitro-salicylic acid, $C_6H_3\left\{\begin{array}{ll}COOH & (1)\\ OH & (2)\\ NO_2 & (4)\end{array}\right.$. The amount of the substance obtained was not sufficient for a careful comparison, but there can be little doubt that it is the acid described by Griess. This transformation is analogous to that of diazo-benzene nitrate into ortho-nitro-phenol,[2] and that of diazo-benzene sulphate into para-phenol-sulphonic acid,[3] under the same conditions.

Decomposition of meta-diazo-benzoic acid sulphate by alcohol.—The sulphate was prepared by the method of Griess,[4] 12 grams being obtained from 10 grams of the metamido acid. 62 grams of the sulphate were decomposed in absolute alcohol in the manner described in the experiment with the ortho-compound. The decomposition began when the temperature of the bath indicated the boiling point of alcohol. If it was lowered to 70° the action stopped. It was necessary to keep it at about 78°, at which point the action took place rapidly. A faint odor of aldehyde was noticed. The excess of alcohol was distilled off after the reaction was finished; the residue was then diluted with water and the contents of the flask distilled in steam. An oil which was heavier than water passed over. The liquid left in the distilling flask was boiled with bone-black, filtered, evaporated, and allowed to stand, but only a small quantity of a tarry oil was thus obtained. The chief product formed was the volatile oil which passed over on distilling with steam. This was found to boil at 213°, and on saponification it gave benzoic acid. The properties of the substance showed conclusively that it is ethyl benzoate. From 62 grams of the sulphate 24 grams of ethyl benzoate were obtained, the yield being 63 per cent. of the theoretical. According to these experiments, therefore, the sulphate of meta-diazo-benzoic acid acts in essentially the same way as the nitrate of ortho-diazo-benzoic acid. Fittica states[1] that when meta-diazo-benzoic acid sulphate is decomposed by alcohol, benzoic acid is obtained. When meta-diazo-benzoic acid sulphate is heated in toluene, decomposition takes place at the temperature of the water-bath, but it was not found possible to isolate any definite substance from the products.

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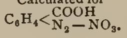
[1] Ber. d. chem. Ges. **11**, 1730.

[2] This Journal **9**, 391.

[3] Ibid. **9**, 393.

[4] Ber. d. chem. Ges. **9**, 1655.

Decomposition of para-diazo-benzoic acid nitrate by alcohol.—The nitrate was made as recommended by Griess.[2] When thrown down suddenly, the compound has much the appearance of light brown sugar. When crystallised from a comparatively dilute solution, the crystals appear as needles, while, when deposited slowly from a considerable quantity of alcohol and ether, it forms thick, colorless, monoclinic prisms, terminated by an orthodome. It is very stable for a diazo-compound, and does not undergo decomposition on standing for several days exposed to the air. Further, it is not decomposed by concussion, but it explodes when heated. It is easily soluble in water, and insoluble in absolute alcohol and in ether. A nitrogen determination of the nitrate was made by boiling with water and collecting the nitrogen given off, with the following result:

	Calculated for  $C_6H_4<^{COOH}_{N_2-NO_3}$.	Found.
N_2	11.60	11.83

24 grams of the nitrate were decomposed as already described.

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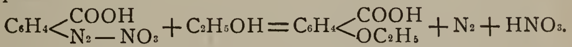
[6] Ber. d. chem. Ges. **11**, 1209.

[2] Ann. Chem. (Liebig), **120**, 126.

The decomposition began at 74° and was complete when the temperature had reached 78°. On treating the resulting liquid as was done in the case of the ortho- and meta-compounds, only a small quantity of oil passed over with water-vapor. This proved to be ethyl benzoate. The principal product was, however, not volatile, and crystallised out of the liquid in the distilling flask. This substance sublimed, forming white leaflets. It was found to be difficultly soluble in water, both cold and hot, and easily soluble in alcohol. It melted at 196°. These properties show that the substance is the para-ethoxy-benzoic acid described by Fuchs[1] and by Ladenburg and Fitz.[2] From 24 grams of the nitrate decomposed, between 9 and 10 grams of the acid were obtained, representing a yield of about 50 per cent. of the theoretical, while only about 2 grams of benzoic acid were obtained. The reaction in this case, then, takes place mainly according to the following equation:



$$C_6H_4\begin{matrix}\diagup COOH \\ \diagdown N_2-NO_3\end{matrix} + C_2H_5OH = C_6H_4\begin{matrix}\diagup COOH \\ \diagdown OC_2H_5\end{matrix} + N_2 + HNO_3.$$

The identity of the acid was proved by a comparison of some of its salts with those described by Ladenburg and Fitz.[2]

The *barium salt*, made by adding barium chloride to a neutral solution of the ammonium salt of the acid, formed very slowly in groups of white scale-like crystals, which were soluble to some extent in cold water and easily in hot water.

The *ammonium salt* is very soluble in water, and was obtained only from concentrated solutions. It crystallises in small white tabular crystals.

The *silver salt*, made by adding silver nitrate to a neutral solution of the ammonium salt, came down at first as a white voluminous precipitate, quite insoluble in cold water and difficultly soluble in hot water. It crystallised from water in needles.

The *lead salt*, made by adding lead acetate to the neutral ammonium salt, was thrown down at once as a white voluminous precipitate, much less soluble in cold water than the barium salt.

The *calcium salt*, made by adding calcium chloride in solution to the neutral ammonium salt, formed very slowly, and only from concentrated solution. The salt formed white needle-like crystals, quite soluble in water.

Decomposition of para-diazo-benzoic acid nitrate by methyl alcohol.—The decomposition began at 57° and was complete at

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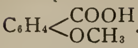
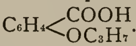
[1] Ber. d. chem. Ges. **2**, 625.

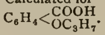
[2] Ann. Chem. (Liebig), **141**, 255.

62°. The product obtained was anisic or para-methoxy-benzoic acid,  $C_6H_4<\substack{COOH\\OCH_3}$. Its melting point was found to be 185°. From 10 grams of the nitrate about 4 grams of the acid were obtained.

Decomposition of para-diazo-benzoic acid nitrate by propyl alcohol.—The decomposition began when the temperature of the bath reached 78° and was complete at 85°. The chief product formed was a crystallised compound which proved to be para-propoxybenzoic acid,  $C_6H_4<\substack{COOH\\OC_3H_7}$. About 6 grams were obtained from 15 grams of the nitrate.

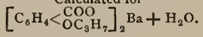
Para-propoxybenzoic acid.—The acid was purified by treatment with bone-black and crystallisation from dilute alcohol. It crystallises in lustrous plates having much the appearance of fish scales. It is practically insoluble in cold water, and with difficulty in hot water; easily in alcohol. It melts at 141.5°–142.5°. It sublimes in thin white plates. An analysis gave the following results:

0.2442 gram substance gave 0.5991 gram CO_2 and 0.145 gram H_2O.

	Calculated for  $C_6H_4<\substack{COOH\\OC_3H_7}$.	Found.
C	66.67	66.91
H	6.67	6.59
O	26.66	...
	100.00	

Barium para-propoxybenzoate, made by adding barium chloride to a solution of the neutral ammonium salt, was thrown down as a white flocculent precipitate, somewhat soluble in cold water, readily soluble in hot water. An analysis gave the following result:

.09 gram substance gave 0.0421 gram $BaSO_4$.

	Calculated for  $\left[C_6H_4<\substack{COO\\OC_3H_7}\right]_2Ba + H_2O$.	Found.
Ba	26.97	26.70

The *silver salt* was made by adding silver nitrate to the neutral ammonium salt. It appeared in the form of a white curdy precipitate, insoluble in cold water, and with difficulty in hot water.

Groups of small needle-shaped crystals were deposited from the solution in water.

The *lead salt*, made by adding lead acetate to the solution of the ammonium salt, was thrown down as a white curdy precipitate, almost insoluble in cold water, readily soluble in hot water. From the solution in hot water it crystallises in small feathery crystals.

The *calcium salt*, made by adding calcium chloride to the solution of the ammonium salt, appeared as a white flocculent precipitate, slightly soluble in cold water, and very readily in hot water. It crystallises in small flocculent crystals from its solution in hot water.

Decomposition of para-diazo-benzoic acid nitrate by water.—The decomposition took place between 80° and 90°. The contents of the flask were filtered to remove a small quantity of a tarry substance, then boiled with bone-black, filtered and allowed to crystallise. In this way, after several crystallisations, two crystallised products were obtained. The one which was formed in larger quantity appeared in granular yellowish crystals melting at 178°. The properties are those of the nitro-oxybenzoic acid described by Max Gruber.[1] Gruber expresses the opinion that his acid is m-nitro-p-oxybenzoic acid, $C_6H_3\left\{\begin{array}{ll}COOH & (1)\\ NO_2 & (3)\\ OH & (4)\end{array}\right.$. On the other hand, the acid of this constitution has been shown by Griess[2] to melt at 185°. The quantity at our disposal was so small as to prevent further purification, and the constitution of the acid cannot be regarded as satisfactorily determined.

The second product of the decomposition of para-diazo-benzoic acid nitrate with water was shown to be para-oxybenzoic acid. It was formed in very small quantity in our experiments, whereas, according to Griess,[3] it is the principal product of this decomposition.

Decomposition of para-diazo-benzoic acid nitrate in toluene.—This decomposition began at 90° and was rapidly completed at the boiling point of water. The action was accompanied by an evolution of nitrogen and the formation of tarry products. After the action was over, the solution in toluene was shaken up with water and barium carbonate, and the toluene then drawn off. A barium salt was found to be in the water solution. After purification of the salt, the acid was separated, and was found to be identical with the nitro acid obtained on decomposing in water. The reaction in toluene is therefore represented in this way:

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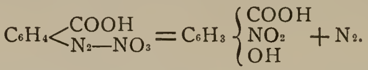
[1] Ber. d. chem. Ges. **12**, 520.

[2] Ber. d. chem. Ges. **20**, 408.

[3] Ann. Chem. (Liebig), **120**, 126.



$$C_6H_4<\begin{matrix}COOH\\N_2—NO_3\end{matrix} = C_6H_3\left\{\begin{matrix}COOH\\NO_2\\OH\end{matrix}\right. + N_2.$$

Comparison of the results obtained in the decomposition of the diazo-benzoic acids by alcohols with those obtained by Griess.—As has been stated, the object of the investigation to which the present communication relates is to determine under what conditions diazo-compounds are decomposed by alcohol in such way that hydrogen takes the place of the diazo-group, and what conditions are favorable to the formation of phenol ethers. This subject had never, so far as appears from the literature, been investigated by Griess, nor does it appear that this chemist ever recognised the possibility of the formation of phenol ethers as a result of the decomposition of diazo-compounds. After the last communication on the subject by one of us (R.) and Orndorff,[1] and after the work described in this paper was completed, Griess[2] published a paper in which he gives the results of experiments on the decomposition of the diazo-benzoic acids by alcohol. In this paper he says that he has long been engaged in this investigation, and that he proposes to continue it. Unfortunately for science this promise was not to be kept, as he died soon afterwards. We should not have done the work described in this paper had Griess' paper been published before we undertook it, and we certainly should not publish our results now, were it not for the fact that in some respects they differ markedly from those described by Griess.

According to this chemist, when ortho-diazo-benzoic acid sulphate is decomposed by alcohol, it is completely converted into benzoic acid, which is obtained directly as such; meta-diazo-benzoic acid sulphate gives benzoic acid and meta-ethoxy-benzoic acid; and para-diazo-benzoic acid sulphate acts like the meta-compound, giving both benzoic acid and para-ethoxy-benzoic acid. We used the nitrate of ortho-diazo-benzoic acid, and obtained ethyl benzoate, with only a very small quantity of benzoic acid. It is possible that the nitrate and sulphate act differently. With the sul-

[1] This Journal **9**, 387.

[2] Ber. d. chem. Ges. **21**, 978.

phate of meta-diazo-benzoic acid we obtained results quite different from those described by Griess. We obtained no benzoic acid, and no ethoxy-benzoic acid, but only ethyl benzoate. We are entirely at a loss to explain the difference, as the work, as nearly as can be judged, was carried on in the same way in both investigations. It would appear, at least, that slight changes in the conditions may cause a very marked difference in the results. Passing now to the para-series, our results with the nitrate are more nearly in accordance with those obtained by Griess with the sulphate, than those in the ortho- and meta-series. We obtained anisic acid with methyl alcohol, para-ethoxy-benzoic acid with ethyl alcohol, and para-propoxybenzoic acid with propyl alcohol. In the decomposition with ethyl alcohol, in which we used a considerably larger quantity of the diazo-compound than in the other cases, a small quantity of ethyl benzoate was obtained.

Influence of the composition, and of the position of groups in determining the course of the action of alcohols on diazo-compounds. —From the results obtained in the study of the decomposition of the three diazo-compounds derived from the toluidines, the conclusion was reached that a methyl-group in the para-position to a diazo-group is favorable to the replacement of this group by hydrogen by treatment with alcohol. Considering now the results described in this paper, it is clear that the influence exerted by the nitro-group is different from that exerted by methyl, and apparently carboxyl acts in still another way. The nitro-group influences the diazo-group whether in the ortho-, the meta-, or the para-position, so that it is replaced by hydrogen. This reaction can only be accounted for by assuming that it is due to the influence of the nitro-group, for it has been shown that when diazobenzene itself is decomposed by alcohol, that is, when the nitro-group is not present in the molecule, the reaction with alcohol takes, for the most part, the other direction. Finally, as regards the influence of carboxyl, our results seem to show that it is exerted upon the ortho- and meta-diazo-groups, causing them to be replaced by hydrogen, while the diazo-group in the para-position undergoes the same reaction as if the carboxyl were not present in the compound. The conclusion is therefore justified that both the position and the character of the groups in the molecule of diazo-compounds exert an influence on the decomposition of the compounds by alcohol.

ON *o*-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

By Ira Remsen and A. R. L. Dohme.

Preparation and Properties of o-Sulphobenzoic Acid.

We have found that this acid can easily be prepared from commercial saccharin in the following way: The commercial product, which, as will be shown in a later article by Mr. W. M. Burton and one of us (R.), consists mainly of benzoic sulphinide and *p*-sulphamine-benzoic acid in nearly equal quantities. When the mixture is boiled with dilute hydrochloric acid, the sulphinide is converted into the acid ammonium salt of *o*-sulphobenzoic acid, while the *p*-sulphamine-benzoic acid is not changed by this treatment. As the acid ammonium salt is easily soluble in water, and *p*-sulphamine-benzoic acid is difficultly soluble, it is only necessary to filter and evaporate to dryness in order to get the ammonium salt. After purification this is dried, and then treated with twice its weight of phosphorus pentachloride. Reaction takes place spontaneously and the mass becomes semi-liquid. When the reaction is complete, the mixture is thoroughly washed with cold water, the chloride remaining as a heavy yellowish oil undissolved. The chloride is then boiled with water until it is decomposed, and the resulting liquid is evaporated to complete dryness to drive off all the hydrochloric acid. The reactions are all quantitative, and the acid thus obtained is pure.

The acid is very easily soluble in water. If its solution is evaporated to a syrupy consistency, it crystallises in long, lathe-shaped, colorless, orthorhombic crystals, which sometimes attain the length of several inches. The faces of the crystals are always etched, a fact which renders a crystallographic examination of them impossible. The accompanying drawing (Fig. 1) shows their general appearance. They are orthorhombic, and usually exhibit only the forms given, viz. $\infty P\breve{\infty}$, ∞P

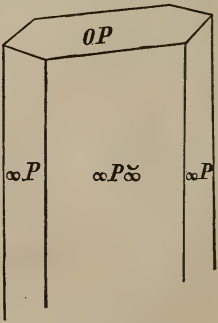


Fig. 1.

and oP, though sometimes there is a macropinacoid ($\infty P\bar{\infty}$) truncating the remaining edges, in which two prismatic faces (∞P) meet. There is a decided cleavage parallel to the best developed face ($\infty P\breve{\infty}$), the brachypinacoid. The acid is slightly hygroscopic. It is very easily soluble in hot and in cold water, but insoluble in ether. It melts at 68°–69°, and solidifies on cooling to a white crystalline mass. If heated for some time at 130°, however, and then allowed to cool, it is found to melt at 130°. This, as will be shown, is due to the fact that the acid when deposited from water solutions contains four molecules of water of crystallisation, and that, when heated at 130°, it becomes anhydrous. Further, when the crystallised hydrated acid is allowed to lie over sulphuric acid in a desiccator for a long time, it loses its water and becomes anhydrous. The analysis of the acid deposited from water gave the following figures:

I. 0.2771 gram gave 0.3046 gram CO_2 and 0.1247 gram H_2O.
II. 0.2855 gram gave 0.3180 gram CO_2 and 0.1295 gram H_2O.
III. 0.3320 gram gave 0.2856 gram $BaSO_4$.
IV. 0.2510 gram gave 0.2083 gram $BaSO_4$.
V. 0.1563 gram lost 0.04076 gram H_2O when heated to 125°.
VI. 0.1278 gram lost 0.0334 gram H_2O when heated to 125°.

	Calculated for $C_6H_4<\begin{smallmatrix}COOH\\SO_2OH\end{smallmatrix}+4H_2O$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	30.66	29.98	30.38	...	...	...	...
H	5.11	5.	5.04	...	...	...	...
O		...	...	...	...	...	...
S	11.68	...	...	11.81	11.39	...	...
H_2O	26.28	...	...	...	...	26.08	26.13

The combustions were made with lead chromate. The sulphur estimations were made by Pearson's method.[1] In determining the water of crystallisation, it was found that three molecules of water are given off at 100°, one half a molecule at 120°, and the last half molecule at about 125°–128°.

When the crystallised acid is kept for some time at 130° a sublimate is formed, which consists of long, thin, white needles, resembling phthalic anhydride. This was supposed to be the anhydride of *o*-sulphobenzoic acid, but analysis showed that it is the acid with two molecules of water.

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[1] Ztschr. anal. Chem. **9**, 271.

I. 0.1322 gram substance gave 0.1732 gram CO_2 and 0.0549 gram H_2O.

II. 0.0903 gram substance gave 0.1179 gram CO_2 and 0.0336 gram H_2O.

	Calculated for $C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2OH} + 2H_2O$.	Found.	
		I.	II.
C	35.29	35.73	35.61
H	4.20	4.61	4.13

The fact that these results, as well as those obtained in the analysis of the acid with four molecules of water, do not more closely agree with the theory is satisfactorily accounted for by the easy solubility of the acid, and hence the difficulty of getting it in perfectly pure condition, and further by the method of forming the sublimed acid. As it is shown that when the hydrated acid is heated for a sufficient length of time to 125°–128° it loses all its water, it is evident that the sublimed acid is the result of an act of dissociation and recombination of the anhydrous acid with water.

o-Sulphobenzoic Anhydride, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>O$.

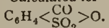
From the experiments above described it appears that even though *o*-sulphobenzoic acid when heated to a sufficiently high temperature may break down into the anhydride and water, these reunite and form a sublimate of the acid. In order to prevent this, the acid, from which the water of crystallisation had been driven off by continued heating at 125° in an air-bath, was mixed with phosphorus pentoxide and this mixture heated. The apparatus used consisted of a small flask of about 75 cc. capacity, through the stopper of which a piece of wide glass tubing a foot long and of an internal diameter of three quarters of an inch was introduced so that about an inch of the tube extended below the lower surface of the stopper into the flask. The mixture of the acid and phosphorus pentoxide was put into the flask and this then introduced into a bath of sulphuric acid, so that the entire body of the flask was immersed and the lower end of the tube reached nearly to the level of the sulphuric acid in the bath. The bath is kept at 130° for several hours, and during this time lustrous, transparent needles and rhombs collect upon and within the lower part of the tube. These crystals sometimes reach the length of an inch. When first taken out they are transparent and limpid like calcite, which they closely resemble, except that they are probably monoclinic. The melting point is 128°. When exposed to the air the crystals quickly become opaque and white. The analysis of the clear crystals just taken from the tube gave the following results:

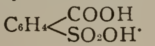
I. 0.1166 gram substance gave 0.1964 gram CO_2 and 0.0253 gram H_2O.

II. 0.0809 gram substance gave 0.1361 gram CO_2 and 0.0173 gram H_2O.

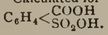
III. 0.2205 gram substance gave 0.2787 gram $BaSO_4$ (by Pearson's method).

IV. 0.2442 gram substance gave 0.3049 gram $BaSO_4$ (by Pearson's method).

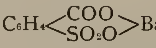
	Calculated for  $C_6H_4<\substack{CO\\SO_2}>O$.	Found.			
		I.	II.	III.	IV.
C	45.65	45.94	45.88	...	...
H	2.17	2.41	2.38	...	...
S	17.39	...	...	17.35	17.14

These results leave no room for doubt that the substance is the anhydride of *o*-sulphobenzoic acid. It was stated above that when the anhydride is left exposed to the air the crystals soon become opaque. Analysis showed that the substance thus formed is the anhydrous acid  $C_6H_4<\substack{COOH\\SO_2OH}$. The following figures were obtained:

0.1635 gram substance gave 0.2476 gram CO_2 and 0.0456 gram H_2O.

	Calculated for  $C_6H_4<\substack{COOH\\SO_2OH}$.	Found.
C	41.58	41.30
H	2.97	3.10

Salts of o-Sulphobenzoic Acid.

Neutral Barium o-Sulphobenzoate,  $C_6H_4<\substack{COO\\SO_2O}>Ba + 2H_2O$. —This was made by boiling a solution of the acid ammonium salt with pure barium carbonate until no more ammonia was detected in the escaping steam. It crystallises from fairly concentrated solutions in beautiful colorless prisms, which are frequently arranged in tufts, and are then elongated in one direction so that they look like needles. Its crystalline form is shown in Fig. 2. It is not quite as easily soluble in water as most of the other salts of the acid. It does not lose all its water of crystallisation until heated to 190°. An optical examination gave the following results:

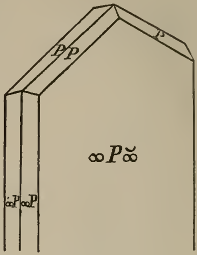


FIG. 2.

System orthorhombic.—Crystals elongated in the direction of the principal axis, and tabular in the plane of the principal and brachy axes. Cleavage parallel to the best developed face, the brachypinacoid ($\infty P\breve{\infty}$).—Axial ratio $a:b:c = .5106:1:.6416$. The angles measured are:

$$\begin{aligned} \infty P \wedge \infty P &= 125° \ 55' \\ \infty P \wedge \infty P\breve{\infty} &= 117° \ 6' \\ P \wedge \infty P\breve{\infty} &= 122° \ 41' \\ P \wedge P &= 114° \ 35' \end{aligned}$$

The extinction is parallel; the plane of the optic axes lies in the brachypinacoid, and the double refraction is weak.

The analysis gave the following results:

I. 0.21935 gram lost 0.0213 gram at 190° and gave 0.1371 gram $BaSO_4$.

II. 0.3175 gram lost 0.0318 gram at 190° and gave 0.1968 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COO}_{SO_2O}>Ba + 2H_2O$.	Found.	
		I.	II.
Ba	36.73	36.75	36.45
H_2O	9.65	9.71	10.02

Acid Barium o-Sulphobenzoate, $\left(C_6H_4<^{COOH}_{SO_2O}\right)_2Ba + 4\frac{1}{2}H_2O$.—This salt was described by Remsen and Fahlberg. They found that it contained two molecules of water of crystallisation, while the analyses given below show that the salt as prepared by us contained four and a half molecules. It was made by boiling the neutral salt with concentrated hydrochloric acid. A mixture of equivalent quantities of barium chloride and the acid salt was thus obtained, and these were separated by repeated crystallisations. The salt crystallises in long, thin, white, silky needles from moderately concentrated solutions. The analysis gave the following results:

I. 0.2416 gram lost 0.0317 gram and gave 0.0916 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2O}\right)_2Ba+4\frac{1}{2}H_2O$.	Found.
Ba	22.10	22.29
H_2O	13.07	13.12

Neutral Calcium o-Sulphobenzoate, $C_6H_4<\genfrac{}{}{0pt}{}{COO}{SO_2O}>Ca+5H_2O$. —This was made by treating finely powdered Iceland spar with a solution of the free acid. After standing for some time over sulphuric acid it crystallises from very concentrated solutions in large, beautiful, colorless, monoclinic prisms, which are, however, much shorter and thicker than those of the neutral barium salt. They are quite efflorescent, and it was therefore impossible to measure the angles. It is more soluble than the barium salt. The analysis gave the following results:

I. 0.2152 gram lost 0.0585 gram at 150° and gave 0.0886 gram $CaSO_4$.

II. 0.2016 gram lost 0.0549 gram at 150° and gave 0.0838 gram $CaSO_4$.

	Calculated for $C_6H_4<\genfrac{}{}{0pt}{}{COO}{SO_2O}>Ca+5H_2O$.	Found. I.	II.
Ca	12.12	12.11	12.22
H_2O	27.27	27.18	27.23

Acid Calcium o-Sulphobenzoate, $\left(C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2O}\right)_2Ca+6H_2O$. —This was made by mixing solutions of equivalent quantities of the free acid and of the neutral salt. It crystallises in short, colorless, monoclinic plates, and is very soluble in water. The analysis gave the following results:

0.1683 gram lost 0.0330 gram at 125° and gave 0.0423 gram $CaSO_4$.

	Calculated for $\left(C_6H_4<\genfrac{}{}{0pt}{}{COOH}{SO_2O}\right)_2Ca+6H_2O$.	Found.
Ca	7.27	7.39
H_2O	19.64	19.61

Neutral Ammonium o-Sulphobenzoate, $C_6H_4<\genfrac{}{}{0pt}{}{COONH_4}{SO_2ONH_4}$. —This was made by neutralising a solution of the acid ammonium salt with ammonia. It crystallises from quite concentrated solutions in colorless, short, thick, lozenge-shaped crystals. The form of the crystals is represented in Fig. 3. An optical examination gave the following results:

System orthorhombic.—The faces $\infty P \bar{\infty}$, $P \bar{\infty}$ and ∞P are equally developed, causing the crystal to assume the lozenge shape. Axial ratio a : b : c = .8904 : 1 : .7125. The angles measured are:

$\infty P \bar{\infty} \wedge P \bar{\infty} = 128° 40'$
$\infty P \wedge \infty P = 83° 23'$
$\infty P \wedge \infty P \bar{\infty} = 137° 48'$

On some of the crystals the basal plane occurs and truncates the edge between the two dome faces ($P \bar{\infty}$). The reflections are not very good.

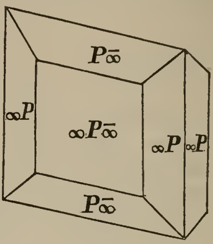


FIG. 3.

The ammonia was determined by Kjeldahl's method, with the results below given:

I. 0.1213 gram gave 0.0173 gram NH_3.
II. 0.1684 gram gave 0.02397 gram NH_3.

	Calculated for $C_6H_4<\begin{matrix}COONH_4\\SO_2ONH_4\end{matrix}$.	Found. I.	II.
NH_3	14.41	14.26	14.23

Acid Ammonium o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix}$. — This salt, as has been repeatedly stated, is formed when benzoic sulphinide is boiled with hydrochloric acid, most readily when the acid is dilute. It has been described and analysed, and its true nature was first recognised by Linn and one of us (R.).[1]

Neutral Potassium o-Sulphobenzoate, $C_6H_4<\begin{matrix}COOK\\SO_2OK\end{matrix} + 2H_2O$.— This was made by neutralising a solution of the acid potassium salt with potassium carbonate. It is more soluble than any of the salts thus far described, and crystallises from very concentrated solutions in concentrically arranged groups of small white needles. An analysis gave the following results:

0.2167 gram lost 0.02397 gram at 180° and gave 0.1190 gram K_2SO_4.

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[1] This Journal **11**, 73.

	Calculated for $C_6H_4<{COOK \atop SO_2OK}+2H_2O$.	Found.
K	24.84	24.62
H_2O	11.46	11.06

Acid Potassium o-Sulphobenzoate, $C_6H_4<{COOH \atop SO_2OK}$.—This salt was first described by Remsen and Fahlberg.[1] It is obtained from the mother-liquors of commercial saccharin, of which it forms, as has been found by Burton and one of us, from 6 to 8 per cent. It crystallises very beautifully.

Neutral Silver o-Sulphobenzoate, $C_6H_4<{COOAg \atop SO_2OAg}$.—This was prepared by boiling a solution of the free acid with an excess of silver carbonate. It is somewhat less soluble than the other salts made. It crystallises well in colorless, short, monoclinic prisms which become dark on exposure to the light. The analysis gave the following results:

I. 0.2177 gram gave 0.1500 gram AgCl.
II. 0.2496 gram gave 0.1720 gram AgCl.

	Calculated for $C_6H_4<{COOAg \atop SO_2OAg}$.	Found.	
		I.	II.
Ag	51.92	51.81	51.81

Silver-ammonium o-Sulphobenzoate, $C_6H_4<{COOAg \atop SO_2ONH_4}$. — This was made by dissolving freshly precipitated silver hydroxide in a solution of the acid ammonium salt. It crystallises in beautiful colorless monoclinic prisms, which closely resemble those of the neutral silver salt. It turns dark if exposed for some time to the light, and decomposes when heated above 130°.

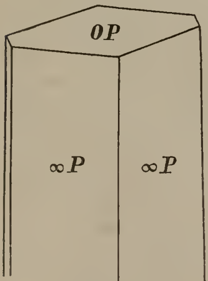

Fig. 4.

An optical examination gave the following results :

System monoclinic.—$\beta = 128° 27'$.—Axial ratio a : b : c = .67228 : 1 : —.[2] The most common forms are oP and ∞ P, while less frequently a small clinopinacoidal face was observed, as shown in Fig. 4. The angles measured are:

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[1] This Journal **1**, 429.

[2] The ratio of c to b cannot be determined, for the reason that no pyramidal or dome faces are present upon any of the crystals of this salt.

$$\infty P \wedge \infty P = 124^\circ\ 27'$$
$$0P \wedge \infty P = 123^\circ\ 23'$$

The analysis gave the figures below :
0.2687 gram gave 0.1192 gram AgCl.

	Calculated for $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{COOAg}\\ \mathrm{SO_2ONH_4}\end{smallmatrix}$.	Found.
Ag	33.13	33.36

Neutral Copper o-Sulphobenzoate, $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{COO}\\ \mathrm{SO_2O}\end{smallmatrix}>\mathrm{Cu} + 3\frac{1}{2}\mathrm{H_2O}$. —The salt was prepared by adding to a solution of the neutral barium salt exactly enough of a solution of copper sulphate to precipitate the barium. It crystallises only from very concentrated solutions, and appears in concentrically arranged groups of fine dark-blue needles. The crystals are quite hygroscopic, and it was hence found difficult to determine the water of crystallisation. Another difficulty which was encountered in making this determination consists in the fact that the salt decomposes at 180° and the last molecule of water is not given off below 170°. The analysis gave the following results:

0.1633 gram lost 0.0309 gram at 170° and gave 0.0312 gram Cu.

	Calculated for $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{COO}\\ \mathrm{SO_2O}\end{smallmatrix}>\mathrm{Cu} + 3\frac{1}{2}\mathrm{H_2O}$.	Found.
Cu	19.37	19.11
$\mathrm{H_2O}$	19.31	18.92

Neutral Magnesium o-Sulphhobenzoate, $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{COO}\\ \mathrm{SO_2O}\end{smallmatrix}>\mathrm{Mg} + x\mathrm{H_2O}$.—This was prepared in the same way as the copper salt. On evaporating the solution the salt is left in the form of a colorless jelly, and it retains this form even after long standing over concentrated sulphuric acid. It is indeed so hygroscopic that unless the sulphuric acid over which it stands is not very concentrated it abstracts water from the acid. It was not analysed.

Chloride of o-Sulphobenzoic Acid, $\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{COCl}\\ \mathrm{SO_2Cl}\end{smallmatrix}$.—The chloride is easily prepared by treating the acid ammonium salt with twice its weight of phosphorus pentachloride. It is a colorless oil insoluble in water. When boiled with water it is slowly decomposed, yielding *o*-sulphobenzoic acid and hydrochloric acid. It dissolves in absolute alcohol with decomposition, and in absolute ether without decomposition. From the solution in ether it crystallises in long, thin, orthorhombic prisms which generally lack the terminal planes. The crystals are represented in Fig. 5.

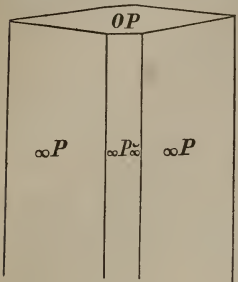

Fig. 5.

An optical examination of the crystals was not possible, because of the unevenness of the planes, due to etching and the action of moisture. The crystals belong to the orthorhombic system, and the forms are ∞P, $\infty P\breve{\infty}$, and oP. The crystals are similar to those of the free acid, but have the prism faces (∞P) best developed, while the latter have the pinacoid faces ($\infty P\breve{\infty}$) best developed. The substance melts at 73°. It was analysed by heating it in a pressure-bottle with water until all the oil had disappeared, and then precipitating with silver nitrate. The following results were obtained :

0.1554 gram gave 0.1868 gram AgCl.

	Calculated for $C_6H_4<\begin{smallmatrix}COCl\\SO_2Cl\end{smallmatrix}$.	Found.
Cl	29.71	29.82

Ethereal Salts of o-Sulphobenzoic Acid.

When the chloride just described is dissolved in cold alcohols the reaction takes place according to the equation :

$$C_6H_4<\begin{matrix}COCl\\SO_2Cl\end{matrix} + ROH = C_6H_4<\begin{matrix}COOR\\SO_2Cl\end{matrix} + HCl.$$

If, however, the solution in an alcohol is boiled, the reaction takes place as represented thus :

$$C_6H_4<\begin{matrix}COCl\\SO_2Cl\end{matrix} + 3ROH = C_6H_4<\begin{matrix}COOR\\SO_2OH\end{matrix} + 2HCl + R_2O,$$

or the chloride, $C_6H_4<\begin{matrix}COOR\\SO_2Cl\end{matrix}$, first formed undergoes change as represented in the equation :

$$C_6H_4<\begin{matrix}COOR\\SO_2Cl\end{matrix} + 2ROH = C_6H_4<\begin{matrix}COOR\\SO_2OH\end{matrix} + HCl + R_2O.$$

Similar changes were observed in the study of the chloride of *p*-nitro-*o*-sulphobenzoic acid.[1]

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[1] See this Journal **11**, 177.

The acid ethereal salts of *o*-sulphobenzoic acid are formed, further, by passing dry hydrochloric acid gas through solutions of the acid in the alcohols. The neutral ethereal salts are made from the silver salts of the acid ethers.

Acid Methyl o-Sulphobenzoate, $C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2OH\end{smallmatrix}$.—This compound is made as above described by boiling the chloride with pure methyl alcohol. It is very easily soluble in water and in alcohol, and cannot be obtained in good crystals. By continued heating on the water-bath with water it is partly saponified.

Barium Methyl o-Sulphobenzoate, $\left(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Ba + 3\frac{1}{2}H_2O$.—This crystallises in concentrically arranged groups of white needles, and is easily soluble in water. The analysis gave these results:

I. 0.1789 gram lost 0.0180 gram at 200° and gave 0.0670 gram $BaSO_4$.

II. 0.1327 gram lost 0.01365 gram at 200° and gave 0.0496 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2O\end{smallmatrix}\right)_2Ba + 3\frac{1}{2}H_2O$.	Found. I.	II.
Ba	21.75	22.02	21.98
$3\frac{1}{2}H_2O$	10.00	10.06	10.29

Silver Methyl o-Sulphobenzoate, $C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2OAg\end{smallmatrix}$.—This generally separates from water as a colorless, thick jelly, which turns dark when exposed to the light. Once it was obtained in crystals which resemble those of the acid potassium salt of *o*-sulphobenzoic acid. The analysis gave these figures:

I. 0.3683 gram gave 0.1651 gram AgCl.

II. 0.2447 gram gave 0.1096 gram AgCl.

	Calculated for $C_6H_4<\begin{smallmatrix}COOCH_3\\SO_2OAg\end{smallmatrix}$.	Found. I.	II.
Ag	33.43	33.71	33.68

Acid Ethyl o-Sulphobenzoate, $C_6H_4<\begin{smallmatrix}COOC_2H_5\\SO_2OH\end{smallmatrix}$. — This closely resembles the corresponding methyl salt. Only the barium salt could be obtained in crystals.

Barium-ethyl o-Sulphobenzoate, $\left(C_6H_4<\begin{smallmatrix}COOC_2H_5\\SO_2O\end{smallmatrix}\right)_2Ba + 4H_2O$, crystallises in groups of colorless needles arranged like rosettes.

I. 0.1790 gram lost 0.0205 gram at 190° and gave 0.0636 gram $BaSO_4$.

II. 0.2138 gram lost 0.0240 gram at 200° and gave 0.0721 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<\substack{COOC_2H_5\\SO_2O}\right)_2Ba+4H_2O$	Found. I.	II.
Ba	20.54	20.89	19.83
H_2O	10.79	11.45	11.23

Dimethyl o-Sulphobenzoate, $C_6H_4<\substack{COOCH_3\\SO_2OCH_3}$. — When silver-methyl *o*-sulphobenzoate is heated with methyl iodide in a pressure-bottle at 100° the dimethyl ethereal salt is obtained. By treating with absolute ether and filtering off the silver iodide, the product separates as a colorless jelly.

Diethyl o-Sulphobenzoate is made in the same way as the dimethyl compound, which it resembles.

Ethyl-methyl o-Sulphobenzoate, $C_6H_4<\substack{COOC_2H_5\\SO_2OCH_3}$. — This compound is made by treating silver-ethyl *o*-sulphobenzoate, $C_6H_4<\substack{COOC_2H_5\\SO_2OAg}$, with methyl iodide. It forms a colorless jelly.

Methyl-ethyl o-Sulphobenzoate, $C_6H_4<\substack{COOCH_3\\SO_2OC_2H_5}$.—This is made like the preceding compound, which it resembles and with which it is isomeric.

Decomposition of the Ethereal Salts by means of Water and Alcohol.—The properties of the four compounds just described are so much alike that the compounds themselves cannot be distinguished from one another. There is no difficulty, however, in distinguishing between them when they are treated with water or with alcohol. The result of this treatment is the breaking off of the alkyl group in combination with the sulphuric acid residue. From the dimethyl ether, therefore, acid methyl *o*-sulphobenzoate was obtained; from the diethyl ether the corresponding ethyl compound. The resulting compounds were easily recognised by means of their barium salts. Further, when the compound, $C_6H_4<\substack{COOC_2H_5\\SO_2OCH_3}$, is boiled with water or with alcohol, the product is acid ethyl *o*-sulphobenzoate, $C_6H_4<\substack{COOC_2H_5\\SO_2OH}$. The barium salt was analysed with the following results:

0.1387 gram gave 0.0496 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<^{COOC_2H_5}_{SO_2O}\right)_2Ba + 4H_2O$.	Found.
Ba	20.54	21.03

Finally, the compound, $C_6H_4<^{COOCH_3}_{SO_2OC_2H_5}$, which is isomeric with the preceding, yields acid methyl *o*-sulphobenzoate, which was identified by means of the barium salt. The analysis gave these results:

0.1102 gram gave 0.0411 gram $BaSO_4$.

	Calculated for $\left(C_6H_4<^{COOCH_3}_{SO_2O}\right)_2Ba + 3\frac{1}{2}H_2O$.	Found.
Ba	21.75	21.93

Action of Phosphorus Pentachloride on Benzoic Sulphinide.

In an investigation on the ethers of benzoic sulphinide, Brackett[1] obtained a product by treating benzoic sulphinide successively with phosphorus pentachloride and methyl alcohol, which he took to be the compound $C_6H_4<^{C(OCH_3)_2}_{SO_2}>NH$. As he worked with very small quantities and was not able to complete his investigation, we continued the work in the hope of clearing up the reaction which takes place between benzoic sulphinide and phosphorus pentachloride. The result was to show that the compound obtained by Brackett was the methyl ether of *o*-sulphamine-benzoic acid. The corresponding ethyl ether was also made.

Methyl o-Sulphamine-benzoate, $C_6H_4<^{COOCH_3}_{SO_2NH_2}$. — This was made exactly according to the directions given by Brackett,[2] and was found to agree with his description. It melts at 124°–125°. Analyses for sulphur and nitrogen resulted as follows:

I. 0.1681 gram gave 0.1848 gram $BaSO_4$.
II. 0.1628 gram gave 0.18137 gram $BaSO_4$.
III. 0.3479 gram gave 0.3868 gram $BaSO_4$.
IV. 0.20385 gram gave 0.01304 gram N (Kjeldahl's method).
V. 0.16705 gram gave 0.01125 gram N (Kjeldahl's method).

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[1] This Journal **9**, 406.

[2] Loc. cit.

	Calculated for $C_6H_4<{}^{COOCH_3}_{SO_2NH_2}$.	Found.				
		I.	II.	III.	IV.	V.
S	14.88	15.09	15.23	14.98	...	...
N	6.51	...	...	...	6.40	6.73

Ethyl o-Sulphamine-benzoate, $C_6H_4<{}^{COOC_2H_5}_{SO_2NH_2}$.—This compound was made in the same way as the methyl ether. It crystallises in beautiful thistle-shaped aggregates of long, white, silky needles which melt at 84°. It dissolves in hot water somewhat more difficultly than the methyl ether, and it melts to a colorless oil before it dissolves. It is easily soluble in alcohol. The analyses gave these results:

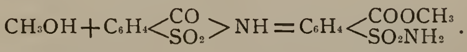
I. 0.2250 gram gave 0.2325 gram $BaSO_4$.
II. 0.1079 gram gave 0.1123 gram $BaSO_4$.
III. 0.13055 gram gave 0.0819 gram N (Kjeldahl's method).
IV. 0.1300 gram gave 0.0821 gram N (Kjeldahl's method).

	Calculated for $C_6H_4<{}^{COOC_2H_5}_{SO_2NH_2}$.	Found.			
		I.	II.	III.	IV.
S	13.97	14.19	14.29	...	...
N	6.11	...	...	6.27	6.31

This ether is identical with the one obtained by Fahlberg and List[1] by treating benzoic sulphinide in alcohol solution with gaseous hydrochloric acid. By way of confirmation both the methyl and ethyl ethers were made by us by this method, and they were found to be identical with the ethers above described. It appears, therefore, probable that when phosphorus pentachloride and alcohol act upon the sulphinide, these react upon each other thus:

$$CH_3OH + PCl_5 = CH_3Cl + POCl_3 + HCl;$$

and that the hydrochloric acid thus liberated acts upon the sulphinide and alcohol, causing them to unite thus:



$$CH_3OH + C_6H_4<{}^{CO}_{SO_2}>NH = C_6H_4<{}^{COOCH_3}_{SO_2NH_2}.$$

The act is plainly analogous to that which takes place when an aqueous solution of hydrochloric acid acts upon the sulphinide, converting it first into *o*-sulphamine-benzoic acid, and then into the acid ammonium salt.

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[1] Ber. d. chem. Gesell. **20**, 1596.

Propyl o-Sulphamine-benzoate, $C_6H_4<^{COOC_3H_7}_{SO_2NH_2}$.— This was obtained as a colorless oil which could not be crystallised.

It will be observed that the melting points of the ethers above described become lower in the order methyl, ethyl, propyl.

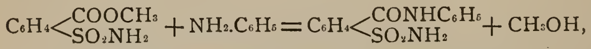
Action of Aniline and of Ortho- and Paratoluidine on the Ethereal Salts of Sulphamine-benzoic Acid, and on Benzoic Sulphinide.

Anilide of o-Sulphamine-benzoic Acid, $C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}$.— By heating either benzoic sulphinide or methyl *o*-sulphamine-benzoate with aniline, the solid dissolves and in the latter case methyl alcohol escapes. On cooling, the mass solidifies. The product was dissolved in water and acidified with hydrochloric acid, when a white crystalline substance separated. This was recrystallised from hot water, in which it is difficultly soluble. It forms short, white, crescent-shaped needles which melt at 189°. The determinations of sulphur and nitrogen gave the following results:

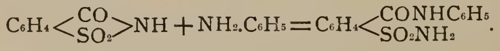
I. 0.1482 gram gave 0.01476 gram N (Kjeldahl's method).
II. 0.1956 gram gave 0.0194 gram N.
III. 0.2017 gram gave 0.02008 gram N.
IV. 0.1300 gram gave 0.11047 gram $BaSO_4$ by Liebig's method.
V. 0.2022 gram gave 0.17267 gram $BaSO_4$.
VI. 0.1419 gram gave 0.11722 gram $BaSO_4$.

	Calculated for $C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}$.	Found.					
		I.	II.	III.	IV.	V.	VI.
N	10.14	9.96	9.91	9.96	...	...	...
S	11.59	...	...	...	11.67	11.72	11.34

The compound is therefore the anilide of the sulphamine acid, and is formed according to the equations:



$$C_6H_4<^{COOCH_3}_{SO_2NH_2} + NH_2.C_6H_5 = C_6H_4<^{CONHC_6H_5}_{SO_2NH_2} + CH_3OH,$$



$$C_6H_4<^{CO}_{SO_2}>NH + NH_2.C_6H_5 = C_6H_4<^{CONHC_6H_5}_{SO_2NH_2}.$$

When boiled with acetic anhydride the anilide gives an acetyl derivative which can be crystallised from water and then appears in the form of beautiful white, satiny needles.

o-Toluide of o-Sulphaminebenzoic Acid, $C_6H_4{<}\substack{CONHC_6H_4CH_3\\SO_2NH_2}$. —Using *o*-toluidine instead of aniline this compound is formed. It is more soluble in water than the anilide, and crystallises from dilute solutions in radially arranged groups of white needles. One recrystallisation suffices to purify it. It melts at 193°. The analysis gave the following figures:

I. 0.15165 gram gave 0.01442 gram N by Kjeldahl's method.

II. 0.1286 gram gave 0.10147 gram $BaSO_4$ by Liebig's method.

	Calculated for $C_6H_4{<}\substack{CONHC_6H_4CH_3\\SO_2NH_2}$.	Found. I.	II.
N	9.66	9.50	...
S	11.03	...	10.84

p-Toluide of o-Sulphamine-benzoic Acid, $C_6H_4{<}\substack{CONHC_6H_4CH_3\\SO_2NH_2}$. —This is very difficultly soluble in water, but easily in alcohol. From the former it crystallises in short white needles which melt at 202°. The analysis resulted as follows:

I. 0.2559 gram gave 0.0239 gram N by Kjeldahl's method.

II. 0.1855 gram gave 0.14897 gram $BaSO_4$ by Liebig's method.

	Calculated for $C_6H_4{<}\substack{CONHC_6H_4CH_3\\SO_2NH_2}$.	Found. I.	II.
N	9.66	9.34	...
S	11.03	...	11.03

Action of Phosphorus Pentachloride on Benzoic Sulphinide at Higher Temperatures.

From a large number of experiments it appears that phosphorus pentachloride does not act upon benzoic sulphinide to form a chloride even at the temperature of 175° if the experiment is performed in an open vessel. If, however, the two substances are heated together to 160° in a sealed tube, action takes place. The product obtained appeared at first as a colorless oil. This is easily volatile with water vapor, and can easily be purified by distilling it in this way. On cooling the oil solidifies, forming a mass of long white needles which melt at 43°. Analysis showed that it contained chlorine and nitrogen, but no sulphur. The properties mentioned are those given by Henry[1] for *o*-chlorbenzonitrile, which he obtained by treating salicylamide or the nitrile with phosphorus pentachloride. That the substance obtained by us is really *o*-chlorbenzonitrile was shown by heating it with dilute hydrochloric acid in a sealed tube, when it is completely converted into *o*-chlorbenzoic acid. This crystallised from water in long, flat, white needles which melted at 136°. The reaction with phosphorus pentachloride then involves the replacement of the sulphone group by chlorine and the elimination of oxygen and hydrogen:

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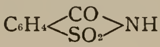
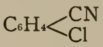
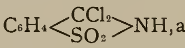
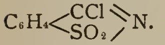
[1] Ber. d. chem. Gesell. 2, 493.


$C_6H_4{<}\substack{CO\\SO_2}{>}NH$


$C_6H_4{<}\substack{CN\\Cl}$.

We should naturally expect to find that the first result of the action of phosphorus pentachloride would be the formation of a chloride of the formula  $C_6H_4{<}\substack{CCl_2\\SO_2}{>}NH$, and the breaking down of this compound by loss of hydrochloric acid to the form  $C_6H_4{<}\substack{CCl\\SO_2}{>}N$. It seems hardly probable, however, in view of the structure of the final product, that the reaction takes place in this way. The reaction is of the same kind as that by which Limpricht and Uslar[1] passed from *m*-sulphamine-benzoic acid to *m*-chlorbenzonitrile. Mr. J. M. Rich is at present engaged in a study of the corresponding para compound, which he has made by treating *p*-sulphamine-benzoic acid with phosphorus pentachloride. Like the isomeric compounds, it is very volatile with water vapor.

JOHNS HOPKINS UNIVERSITY, CHEMICAL LABORATORY, *May*, 1889.

THE DISSOCIATION OF THE SULPHIDES OF CADMIUM AND ZINC BY MEANS OF METALLIC CADMIUM AND ZINC.

BY H. N. MORSE AND J. WHITE, JR.

In a former communication[2] we suggested that the transportation in a current of hydrogen of the oxide of zinc and of the sulphides of zinc and cadmium, which was observed by Deville, was not due, as he supposed, to a *reduction* with formation of water and the sulphide of hydrogen, and a subsequent decomposition of these compounds by the metals, but rather to a *dissociation* of the oxide and of the sulphides under the influence of the hydrogen, and a reunion of the dissociated constituents of these compounds in other parts of the tube.

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[1] Ann. Chem. (Liebig) **106**, 35.

[2] This Journal **11**, 260.

The intermediate formation of water and of sulphide of hydrogen, especially the latter, seemed to us improbable, for reasons which were there given. It appeared more probable that the attraction of the hydrogen for the oxygen and the sulphur so diminished the stability of the compounds that they dissociated at the prevailing temperature into their elements; that these, unable to recombine as long as the conditions under which the dissociation was effected were maintained, passed along together until other conditions permitting of their reunion were found.

Representing the two views by equations, we have:

I.

$$\begin{array}{ll} \text{1st.} & \left.\begin{array}{l} ZnO + H_2 = H_2O + Zn \\ ZnS + H_2 = H_2S + Zn \\ CdS + H_2 = H_2S + Cd \end{array}\right\} \text{at the lower temperature.} \\ \text{2d.} & \left.\begin{array}{l} Zn + H_2O = ZnO + H_2 \\ Zn + H_2S = ZnS + H_2 \\ Cd + H_2S = CdS + H_2 \end{array}\right\} \text{at the higher temperature.} \end{array}$$

II.

$$\begin{array}{ll} \text{1st.} & \left.\begin{array}{l} ZnO + xH_2 = Zn + O + xH_2 \\ ZnS + xH_2 = Zn + S + xH_2 \\ CdS + xH_2 = Cd + S + xH_2 \end{array}\right\} \begin{array}{c}\text{probably at the higher} \\ \text{temperature.}\end{array} \\ \text{2d.} & \left.\begin{array}{l} Zn + O + xH_2 = ZnO + xH_2 \\ Zn + S + xH_2 = ZnS + xH_2 \\ Cd + S + xH_2 = CdS + xH_2 \end{array}\right\} \begin{array}{c}\text{probably at the lower} \\ \text{temperature.}\end{array} \end{array}$$

We then suggested, as probably true, the general proposition that when two substances, one a compound and the other something which has an affinity for one of the constituents of the same, are brought together, the stability of the compound is so diminished that it will dissociate at lower temperatures than in the absence of the substance which exerts an attraction upon one of its constituents, and that recombination cannot take place as long as the conditions resulting in dissociation continue.

Such a fact would accord well with what appears to be the most reasonable explanation of those phenomena which we are accustomed to classify under the names of *mass*, *catalytic*, and *contact* action. Indeed, it would be, according to the circumstances, the *extreme phase* of *mass* or of *catalytic action*. It would also explain, in part at least, certain facts connected with the combination of gases, such as the impossibility of exploding a mixture of certain proportions of oxygen and hydrogen.

The dissociation of chemical compounds by one of their own constituents in the free state is involved in the proposition, and it appeared advantageous to begin the attempt at experimental demonstration at that point, because by so doing we should avoid the doubt which would pertain to the results if the formation of new and intermediate compounds were possible, as in the experiments of Deville.

In the first communication we described the dissociation of the oxides of zinc and cadmium by means of their respective metals. We now have to describe a similar dissociation of the sulphides of the same elements.

The pure sulphides were prepared by dissolving the metals, which had been repeatedly distilled in a vacuum,[1] in hydrochloric acid, and precipitating by sulphide of hydrogen obtained from the sulphide of barium. Acetate of sodium was added to the solution of zinc. The precipitates were washed for several days with water containing sulphide of hydrogen, with use of the filter pump. They were then dried at 100°, and afterwards heated for several hours to about 300° in a current of pure and dry sulphide of hydrogen. Finally, to remove any free sulphur which might be present, they were treated for six hours with sulphide of carbon in a Soxlet's extraction apparatus.

The dissociation of the sulphides was effected by the method which was employed in the dissociation of the oxides; their stability in a vacuum having first been demonstrated by heating the exhausted tubes containing them to a temperature at which the glass softened and collapsed. No signs of volatility could be detected. In all subsequent experiments, mixtures of about 15 grams of the sulphide and about 40 grams of the metal were employed.

The phenomena which presented themselves, when the exhausted tubes containing the mixture of sulphide and metal were heated in the furnace, were similar to those observed during the dissociation of the oxides. Soon after the metal had fused, a yellowish white film formed upon the interior of the cool portion of the tube just outside of the furnace. This film was supposed to be sulphur, and its appearance in that position is to be explained in the same way as the considerable evolution of free oxygen during the early period of the dissociation of the oxides; that is, while the tube is still comparatively free from the vapors of the metal, the sulphur liberated by dissociation, having a higher rate of diffusion than the metal, would naturally escape, in part, and deposit itself in the locality where the formation of the film was observed. Later in the experiments the appearance of these films changed to that of the sulphides. As the temperature of the mixture rose, a deposit of sulphide was observed to form upon the bottom and the top of the tube in front of the dam. This, as in the case of the oxides, was driven farther forward by the distilling metal, and deposited again as a long line of crystals upon the bottom of the tube. But the sulphides which were deposited in the heated portion of the tube in front of the dam did not, like the oxides, entirely disappear before the distilling metals. In the case of the zinc, but little of the sulphide was carried into the cool portion of the tube lying beyond the furnace. The sulphide of cadmium was transported farther and in much larger quantities than the sulphide of zinc. In the cool portion of the tube beyond the furnace its crystals could be seen to form and fall in a manner resembling a fine rain. By rapidly raising the temperature the sulphide of cadmium may be made to dissociate with almost explosive violence. In this way, on several occasions when the sulphide and its metal were not so distributed behind the dam as to leave considerable free space between it and the top of the tube, the material was blown through the entire length of the tube into the pump.

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[1] This Journal **10**, 312.

The dissociation of the oxides appears to begin at a somewhat lower temperature than that of the sulphides. Of the two oxides, the oxide of zinc appears to dissociate the more readily; of the two sulphides, the sulphide of cadmium.

Chemical Laboratory, Johns Hopkins University.

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM ZINC.

By Edgar F. Smith and Lee K. Frankel.

The separation of these metals has been effected by Yver,[1] who employed the acetates for this purpose. Eliasberg[2] and Smith and Knerr[3] confirmed this observation, at the same time emphasising the fact that the current should be carefully regulated, otherwise unsatisfactory results would be obtained. A solution, containing cadmium and zinc as tartrates together with free tartaric acid, will also yield all its cadmium to a current generating 0.4–0.5 cc. oxy-hydrogen gas per minute.[4] We have no record of other salts of these metals having been used for their electrolytic separation, and therefore have taken occasion to learn what might be the result with solutions of the double cyanides, such as we employed in separating mercury and copper.[5]

Beilstein and Jawein[6] have shown that both cadmium and zinc can be completely precipitated from a cyanide solution, but have not given the current strength employed by them in their experiments, nor did they attempt the separation of these metals from each other.

As our experience with mercury and copper clearly indicates, it is frequently possible by close attention to the current to effect electrolytic separations which ordinarily seem impossible. With this fact clearly before us, our first work, with the metals now under consideration, was to ascertain how feeble a current would suffice for the complete deposition of each metal, when alone in a cyanide solution, in the presence of an excess of an alkaline cyanide. We very soon discovered that the cadmium separated readily and with a much weaker current than was necessary for the deposition of the zinc. The latter will, however, separate from a cyanide solution, even under the influence of a feeble current, but not until the excess of cyanide has been completely decomposed. With the quantity of cyanide used by us, and with a current of the strength indicated below, this complete decomposition of the alkaline cyanide is not likely to occur in a shorter period than forty-eight hours. Hence it follows, that as the quantity of cadmium used in our experiments is entirely precipitated in a little more than eighteen hours, the complete separation of cadmium from zinc is thoroughly feasible by this method.

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[1] Bull. Soc. Chim. de Paris **34**, 18.

[2] Ztschr. anal. Chem. **24**, 548.

[3] This Journal **8**, 210.

[4] This Journal **8**, 210.

[5] Journal Franklin Institute **127**, 469, and this Journal **11**, 264.

[6] Ber. d. chem. Ges. **12**, 446, 762.

All our experiments were conducted in the cold, and care was taken in each case to examine the deposited metal for zinc, and the residual solution for cadmium. The conditions under which our work was carried out and the results obtained are these:

Metallic Cadmium in grams.	Cadmium Found.	Metallic Zinc present.	Difference in per cent. of Cadmium.	KCN in grams.	Total Dilution.	Current in cc. of O=H Gas.	Time.
.1817	.1813	...	—.22	4.5 grams in each separation.	200 cc.	.3 cc in each experiment.	18–23 hours.
	.1818	...	+.05				
	.1815	...	—.11				
	.1822	...	+.22				
	.1812	.2000	—.27				
	.1818	"	+.05				
	.1828	"	+.60				
.2426	.2422	...	—.16				
	.2432	...	+.24				
	.2426	...	...				
	.2420	.2000	—.24				
	.2435	"	+.30				
	.2429	"	+.12				
	.2426	"	...				
	.2433	"	+.28				
	.2434	"	+.32				

The cadmium deposit was light gray in color and crystalline in structure. It was washed with hot water and dried upon a warm iron plate.

CHEMICAL LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA., *May* 21, 1889.

OF THE SOLUBILITY OF THE CONSTITUENTS OF SEEDS IN PREPARED SOLUTIONS OF PTYALIN, PEPSIN AND TRYPSIN.

By W. Maxwell.

Supplementary to a study of the constitution of the legumes—Pisum sativum, Faba vulgaris, and Vicia sativa—experiments were conducted by the author in the Agricultural-Chemical Laboratory of the Zürich Polytechnic, by way of approaching a knowledge of the action of the animal solvents upon the several groups of plant constituents, and of the total solubility of each respective seed.

The investigations were pursued according to a generalisation of the methods adopted by Prof. Stutzer[1] in his valuable studies on artificial digestion.

Prof. Stutzer found that the mean of solubility of the nitrogenous constituents of vegetable substances was obtained by the consecutive treatment of the substance with solutions of gastric juice (pepsin) and pancreatic juice (trypsin).

The mean digestibility of the non-nitrogenous matters is consequent upon treatment with ptyalin (diastase solution may replace ptyalin),[2] pepsin and trypsin in the natural order in which these solvents operate in the animal system.

These experiments were conducted as follows: A considerable quantity of material (50–100 grams) was treated with a solution of diastase until wholly free from starch and the substance gave no further color reaction with iodine. The residue was thoroughly washed out, dried, and weighed.

Of the diastase residue, a given weight (about 2 grams) was treated with a solution of pepsin. The undissolved residue was washed out, dried, and weighed. The nitrogen remaining in the pepsin residue was determined according to the method of Kjeldahl.

A second quantity of the diastase residue was digested consecutively with solutions of pepsin and trypsin, and the undissolved residue treated precisely the same as the pepsin residue.

The pepsin solution was prepared according to the notes of Stutzer, and the solution of trypsin as given by Haidenhain.[3] The estimations are calculated upon material dried at 100° C.

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[1] Ztschr. phys. Chem. **12**, Heft I, II, 1887.

[2] Ibid.

[3] Pflügers Archiv **10**, S. 582 und 576.

Pisum sativum.

		Dissolved.
Original material	64.43 grams.	
(1) After treatment with diastase	25.50	58.87 per cent.
(2) After further treatment with pepsin	9.47	24.87
(3) After further treatment with trypsin	7.30	5.99
Total solubility		89.73

The original material contained 4.151 per cent. of nitrogen. After digesting the diastase residue with pepsin, the undissolved nitrogen in the residue, in proportion to the total nitrogen, was 0.143 per cent. The second quantity of diastase residue, which had been digested with pepsin and trypsin consecutively, a nitrogen determination of the final residue yielded only 0.091 per cent. Solubility of the total nitrogen = 97.77 per cent.

The solubility of the nitrogenous bodies we are not able, with even approximate certainty, to deduce from the percentage of the total nitrogen dissolved. The nitrogen in vegetable organisms is distributed in combinations, certain of which the molecular structure and value is not known. If, however, in order to form, for the present, an approximate judgment of the comparative solubilities of the nitrogenous and non-nitrogenous constituents, we consider the nitrogen dissolved as expressing the amount of the soluble nitrogenous bodies, the solubility of the non-nitrogenous substances may be calculated by difference, and in the example of Pisum sativum the amount was found to be 91.95 per cent.

The undissolved residue of the seed appears as follows:

Insoluble nitrogenous matter	2.22 per cent.
Insoluble non-nitrogenous matter	8.05
	10.27

Faba vulgaris.

		Dissolved.
Original material	80.04 grams.	
(1) After treatment with diastase	34.10	57.39 per cent.
(2) After treatment with pepsin	11.89	24.77
(3) After treatment with trypsin	10.36	3.65
Total solubility		85.81

	Dissolved.
Total nitrogen contained in original material	4.477 per cent.
After digesting the diastase residue with pepsin	0.239
After digesting the diastase residue with pepsin and trypsin	0.160
Solubility of total nitrogen—nitrogenous bodies (?)	96.43 per cent.
Solubility of non-nitrogenous bodies	89.38
Insoluble nitrogenous matter	3.57 per cent.
Insoluble non-nitrogenous matter	10.62
	14.19

Vicia sativa.

Original material	90.94 grams.	
(1) After treatment with diastase	39.80	56.23 per cent.
(2) After treatment with pepsin	13.41	28.96
(3) After treatment with trypsin	11.59	2.04
Total solubility		87.23

Total nitrogen in the original material	5.039 per cent.
After digesting the diastase residue with pepsin	0.291
After digesting the diastase residue with pepsin and trypsin	0.255
Solubility of total nitrogen—nitrogenous bodies (?)	94.95 per cent.
Solubility of non-nitrogenous bodies	92.26
Insoluble nitrogenous matter	5.03 per cent.
Insoluble non-nitrogenous matter	7.74
	12.77

An experiment was made in order to observe the digesting effect of pepsin by direct treatment of the original material. It was found, in the example of Faba vulgaris, that only some 32 per cent. of the total seed-matter was dissolved, of which 25.23 per cent. consisted of the albuminoids. The result was so remarkable that some doubt appeared to be involved, and a nitrogen determination of the residue was made in order to be sure that the solvent had been operative.

Nitrogen contained in the residue	0.240 per cent.
Previous nitrogen contained in pepsin residue of the same seed	0.239

It appears from these experiments that the starch contained in the seeds not only remains undissolved, it also exercises a preventive effect upon the digestion of the other insoluble carbohydrates (paragalactine, etc.). This observation is in support of Stutzer's sequence of solvents by which the mean solubility of the non-nitrogenous substances is effected.

It is of interest to observe from the above tables the action of pancreatic juice upon the nuclein bodies which had been liberated from their albuminoid combinations (nuclein albumines) by the preceding digestion with pepsin. These bodies (nucleins), which remained intact under the protracted action of the acid pepsin solution, yielded up a considerable portion of their nitrogen to digesting with an alkali solution of trypsin.

It may here be in place to call attention to a general error attaching to the estimation of albuminoids by means of the common methods. The "nucleins" are insoluble in water, consequently they are not removed with the soluble nitrogenous compounds, but are contained in the albuminoid precipitates and necessarily in the nitrogen determination. Where the error has not been allowed, in more strictly scientific studies, the albuminoid estimations will be found too high, and in proportion to the amounts of nucleins present.

The results obtained by artificial methods of digestion, and the data gathered from trials with living animals, indicate such a measure of agreement as to confirm the value of laboratory experiment. In certain cases living tests have given higher results than artificial experiment. The contrary is, however, the more general, or the rule. And this fact has been understood from the consideration that larger amounts of food-matters are served to animals than the juices of the system are capable of reducing to the absolute degree of solubility. Proofs of this occur frequently in the instances of animals (pigs and fattening cattle) which are being fed with a very concentrated diet. In examples where animal digestion has given higher results than artificial experiment, the results have been considered in relation to the supplementary action of micro-organisms in digestion processes. The investigations conducted by Stutzer artificially, and by Prof. Pfeiffer with living animals, are valuable contributions to this subject.[1]

HARVARD COLLEGE LABORATORY.

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[1] Ztschr. phys. Chem. 9, 213.

NOTES.

On Allotropic Forms of Silver.

M. Carey Lea has just given an account of three allotropic forms of silver. The following quotations from the original article[1] will give a general idea of the character of his results:

"Silver is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in color and lustre. . . . These allotropic forms of silver are broadly distinguished from normal silver by color, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerised form. Something analogous has already been observed with other metals, lead and copper. . . . The forms of allotropic silver which I have obtained may be classified as follows:

"*A.* Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

"*B.* Insoluble, derived from A, dark reddish brown while moist, when dry somewhat resembling A.

"*C.* Gold silver, dark bronze whilst wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-colored. Insoluble in water, appears to have no corresponding soluble form.

". . . All these forms have several remarkable properties in common:

"1. *That of drying with their particles in optical contact, and consequently forming a continuous film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a lustre as high as that of metallic leaf. C, when so treated, would be taken for gold leaf. But this property is much better seen by brushing the substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is good. A and B form bluish-green mirrors, C gold or copper-colored mirrors.

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[1] American Journal of Science **37**, 476 (1889).

"2. *The halogen reaction.*—When any of these allotropic forms of silver are brushed over paper and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colorations are obtained. . . . . With sodium hypochlorite the colors are often magnificent, intense shades with metallic reflections, reminding one of the colors of a peacock's tail. . . .

"3. *The action of acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal gray silver; even acetic acid, not too much diluted, does this.

"4. *Physical condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces and by moderate trituration yield a fine powder."

When dilute solutions of ferrous citrate and of a silver salt are brought together a deep red liquid is formed. If the solutions are concentrated the liquid turns almost completely black. In the latter case a precipitate of a fine lilac-blue color is formed. This precipitate is insoluble in several saline solutions, but it dissolves easily in pure water with an intense red color. Analysis of this precipitate showed that it contained 97.27 per cent. of silver and no hydrogen nor oxygen, the remaining 2 or 3 per cent. being fully accounted for by ferric oxide and citric acid present as impurities. The solution formed in water was examined optically and found to be a true solution. The substance, when treated with mercury, amalgamates by simple friction. The author says: "If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself."

The insoluble form B is obtained by adding certain neutral salts to the solution of the soluble form A above described. Among the salts which may be used for this purpose are magnesium sulphate, cupric sulphate, ferrous sulphate, etc. The insoluble form is purple brown, and "by repeated washing, by decantation or otherwise, continually darkens." It is curious "that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution; potassium and sodium sulphate produce a yellowish red solution, and ammonium sulphate a red one. None of these solutions has the same blood-red color as the original solution; the form of silver seems to change with the slightest change of condition." The analysis of this substance showed that it contained 97.96 per cent. of silver, and that the remaining 2.04 per cent. consisted of ferric oxide and citric acid.

The gold-yellow and copper-colored silver (C) is obtained in the following way: "Two mixtures are to be prepared: No. 1, containing 200 cc. of a ten per cent. solution of silver nitrate, 200 cc. of a twenty per cent. solution of Rochelle salt, and 800 cc. of distilled water. No. 2, containing 107 cc. of a thirty per cent. solution of ferrous sulphate, 200 cc. of a twenty per cent. solution of Rochelle salt, and 800 cc. of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which in the filter has a beautiful bronze appearance. After washing it should be removed whilst in a pasty condition and spread over watch-glasses or flat basins and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. . . . Although the gold-colored silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water; this is essential. It dries into lumps exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. . . . When the thick pasty substance is extended over glazed paper, it dries with the splendid lustre of gold leaf, with this essential difference, that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clear glass, beautiful gold-colored mirrors are obtained. The film seems to be entirely continuous."

The analysis of the gold-colored variety showed that it contained 98.75 per cent. silver, and that the residue was almost wholly ferric tartrate. I. R.

Determination of Iron in the presence of Hydrochloric Acid by means of Permanganate of Potassium.

In 1884, C. Reinhardt published an account of a method for the determination of iron which consisted of the following operations: 1st, reduction of the hot ferric chloride by means of stannous chloride; 2d, conversion of the excess of stannous chloride into stannic chloride by means of mercuric chloride; 3d, addition of manganese sulphate to the greatly diluted solution; 4th, titration with permanganate.

The solution becomes yellow in consequence of the formation of ferric chloride; and finally, when the oxidation is complete, it changes to a brown instead of a rose color. The detection of the end of the reaction is thus rendered somewhat difficult. But Reinhardt finds that this difficulty may be wholly avoided by the addition of phosphoric acid. The solution then remains colorless, and the completion of the oxidation is indicated by the appearance of the pure rose-color.

The solutions employed are:

1st. 6 grams of permanganate dissolved in 1000 cc. of water and standardised by tetraoxalate of potassium.

2d. 200 grams of manganese sulphate dissolved in 1000 cc. of water to which a few cubic centimeters of diluted sulphuric acid have been added; 1000 cc. phosphoric acid, specific gravity 1.3, diluted with 600 cc. of water and carefully mixed with 400 cc. of sulphuric acid, specific gravity 1.8. The manganese sulphate and phosphoric acid solutions, when the latter has cooled down, are mixed together. Amount required for a single determination, 60 cc.

3d. 50 grams of mercuric chloride dissolved in 1000 cc. of water. Amount required for a single determination, 60 cc.

4th. 120 grams of tin free from iron dissolved in 500 cc. of hydrochloric acid, specific gravity 1.19. After allowing the hydrochloric acid and tin to act for some time in the cold, the solution is completed by warming on the water-bath. The solution is then diluted to 1000 cc. with water, and filtered through asbestus free from iron into a mixture consisting of 2000 cc. of water and 1000 cc. of hydrochloric acid, specific gravity 1.124. Each cubic centimeter is equivalent to 0.020 gram of iron.

0.5 to 1.0 gram of the material previously roasted, if necessary to oxidise sulphur, carbon or organic matter, is dissolved with heat in 25–30 cc. of hydrochloric acid, specific gravity 1.19. This solution is treated with the solution of stannous chloride until it becomes colorless, then with 60 cc. of the solution of mercuric chloride. Its volume is finally increased to 1500 cc. by the addition of water faintly reddened with permanganate and containing 60 cc. of the solution of manganese sulphate and phosphoric acid. In this way a sharply defined end-reaction is obtained.

The quantity of permanganate required to redden the water employed in diluting to 1500 cc. is subtracted, in calculating the results, from the total quantity of permanganate used.—(*Chem. Zeit.* **13**, 323.)

G. A. Krauss.

ERRATUM.

Page 488 (Vol. X, No. 6). In the second part of the table beginning with "Bread," the column headed "Fat" should have been headed "Nitrogen-free extract," and *vice versa.*

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DYNAMICAL THEORY OF ALBUMINOID AMMONIA.[1]

By Robert B. Warder.

The following investigation was suggested by committee work of the American Association for the Advancement of Science, on water analysis. It is an attempt to apply well established principles of mass action to certain questions involved in the determination of albuminoid ammonia. The following points have been kept in view:

1. Can some probable correction be made for the error incurred by stopping the distillation while ammonia is still coming off?
2. What modification of the original method seems rational?
3. What insight can be gained into the nature of the chemical process?

The experimental basis of the following paper will be found in Mallet's report on the determination of organic matter in potable water,[2] with the addition of some details kindly communicated by Dr. Charles Smart.

I. *Distillation of Free Ammonia.*

In the distillation of albuminoid ammonia, two stages must be distinguished: first, oxidation of the nitrogenous body by the alkaline solution of permanganate; and, second, the separation of ammonia thus formed by distillation. It will be most convenient to begin with the discussion of this second process, which is essentially physical. As in any other case of fractional distillation, water and ammonia both pass from the fluid to the gaseous or vapor condition, in accordance with their respective tensions and mass.

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[1] Prepared for the Toronto meeting of the American Association for the Advancement of Science.

[2] Report of the National Board of Health for 1882.

Let $x =$ volume of fluid in retort,
$y =$ weight of ammonia in retort,
$z =$ weight of ammonia in distillate.

Then $\frac{y}{x} =$ concentration of fluid in retort,
$\frac{dy}{dx} = \frac{-dz}{dx} =$ concentration of any small portion of distillate.

The coefficient of volatility may be defined as the ratio of the concentration in any small portion of distillate to that of the fluid in retort. Designating this coefficient as k,

$$\frac{dy}{dx} = k \, . \, \frac{y}{x}. \tag{1}$$

In the ordinary distillation of ammonia, k is found to be approximately constant, and it will be so regarded here. By integration,

$$\log_e y = k \, . \log_e x + \text{constant};$$

using zero subscript to denote initial conditions,

$$\log_e y_0 = k \, . \log_e x_0 + \text{constant},$$

$$\therefore \quad \log_e \frac{y}{y_0} = k \, . \log_e \frac{x}{x_0},$$

or

$$\log \frac{y}{y_0} = k \, . \log \frac{x}{x_0}, \tag{2}$$

a very useful formula for determining the coefficient of volatility and tracing the progress of distillation. Curve *A*, in the figure, represents y as that function of x defined by equation (2).

Wanklyn,[1] who was the first to use and define the term coefficient of volatility, reports four experiments for its determination. One liter of dilute aqueous ammonia was distilled in each case until 50 cc. of distillate had been collected. As nearly one-half the ammonia taken was distilled with the first 5 per cent. of water (the concentration in the retort being gradually reduced at the same time), Wanklyn estimated k equal to "about thirteen or fourteen." The experimental data are given below with more precise values of k, as calculated by equation (2). In each case, $x_0 = 1000$, $x = 950$. The quantities of ammonia taken, and that found in the distillate, are expressed in milligrams under y_0 and z respectively; the difference (remaining in retort) under y:

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[1] Phil. Mag. [4], **45**, 132 (Feb. 1873).

y_0.	z.	y.	k.
1000	480	520	12.74
1	.50	.50	13.50
.5	.235	.265	12.39
.2	.095	.105	12.55
			Mean = 12.8

This value may be rather too low, as no account is taken of a possible loss from imperfect condensation, a loss averaging 7.2 per cent. in Smart's experiments.

The same author observes also[1] that in the distillation of one-half liter of water, the ammonia found in the first measure of 50 cc. is three-fourths of the whole quantity of ammonia obtained. By equation (2), assuming that any loss affects each part in the same proportion,

$$\log \tfrac{1}{4} = k \,.\, \log \tfrac{9}{10},$$

$$\therefore \quad k = 13.14.$$

Thirty experiments by Smart to determine the loss of ammonia by imperfect condensation are also available for the estimation of k, the successive measures of distillate having been nesslerised separately.[2] A single distillation affords several values, as each fraction determined may be compared with the whole quantity found in subsequent fractions. The values thus deduced vary from 10 to 16, with a few instances beyond these extremes. The variations in the values of k do not show any well marked relation to the whole quantity of ammonia present, to the amount of loss, nor to the rate of boiling. The experimental work was done wholly for another purpose, and probably with just such care as the conscientious analyst would ordinarily give. We may then assume 13 as a mean value for k, remembering that considerable allowance must be made for unexplained variations.

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[1] Wanklyn's *Water Analysis*, 6th and 7th editions, p. 41.

[2] Most of these data appear in the Report of the National Board of Health for 1882, pages 312-314.

II. *Application of Formula to Estimation of Free Ammonia.*

In the analytical process it is usual to distill three or four fractions, each nearly equal to one-tenth of the original volume. For 100 parts of free ammonia present, when $k = 13$, theory would lead us to expect, in four successive fractions, the increments named below under Δz, with loss of 0.13; vertical lines in the figure, a, a, a, represent these increments geometrically. The ratio of each increment to the next is stated under r. The mean values of the ratios obtained in the experiments to determine loss of ammonia are given under r':

No.	Δz.	r.	r'.
1	74.6	3.75	4.23
2	19.9	4.4	5.26
3	4.53	5.4	5.65
4	.84		

In the analyses of natural waters reported (*loc. cit.* pp. 321–330), considerable variation appears in the ratios of successive increments, but usually not more than might be expected from the observed variations in k. Analyses No. 18 and No. 54 are exceptional and happen to give identical results, the free ammonia being .015, .01, and .01 mgm. in the three fractions nesslerised, with ratios 1.5 and 1. In such cases there is a strong probability that some more complex body is gradually decomposed by simple boiling with sodium carbonate. Small ratios between the successive fractions of "free ammonia" may lead to suspicion of urea contamination, though of course due caution should be used in drawing such conclusions. The analyst will at least find it instructive to enter the ratios in his note-book, together with the separate results of nesslerising; this will appear more plainly in the following sections. The slowness of the chemical action usually retards the distillation of albuminoid ammonia, giving rise to much smaller ratios between successive fractions than those named above.

III. *Action of Mass in Formation of Albuminoid Ammonia.*

We must now attempt to follow the chemical as well as the physical aspect of the process. In the former the reactions may be much involved, and various formulas may be required to represent the successive formation and destruction of different substances. Let us consider, as an ideal case, a single chemical reaction, involving one molecule each of three reacting bodies; the formation of ammonia taking place at each moment of distillation, in each cubic centimeter of the fluid, in proportion to the product of the quantities of the nitrogenous body, the potash, and the permanganate present therein.

Retaining the use of x, y, and z as explained in section I, let
$u =$ weight of the nitrogenous body in the retort,
$v =$ weight of potash in the retort,
$w =$ weight of potassium permanganate in the retort,
$t =$ time, in minutes, from the beginning of the reaction,
$a =$ coefficient of speed.

Assume also a uniform rate of distillation, in which
$b =$ volume distilled per minute,
$bc =$ volume of fluid in retort at the beginning of the action;

whence

$$x = bc - bt,$$

and

$$dx = -bdt.$$

Then $\frac{u}{x}$, $\frac{v}{x}$, and $\frac{w}{x} =$ weights of the three active substances in each cubic centimeter of fluid in the retort,

$$\frac{-du}{dt} = b\,\frac{du}{dx} = \text{rate of change},$$

and, by the law of mass action,

$$b\,\frac{du}{dx} = a\,.\,\frac{u}{x}\,.\,\frac{v}{x}\,.\,\frac{w}{x}\,.\,x = avw\,.\,\frac{u}{x^2},$$

$$\therefore \quad \frac{du}{u} = \frac{avw}{b}\,.\,\frac{dx}{x^2}. \tag{3}$$

The reagents are present in such large excess that v and w may be regarded as constants (unless the permanganate suffers from an unusual amount of pollution), and by integration,

$$\log_e u = -\frac{avw}{b}\,.\,\frac{1}{x} + \text{constant},$$

$$\log_e u_0 = -\frac{avw}{b}\,.\,\frac{1}{x_0} + \text{constant},$$

$$\therefore \quad \log_e \frac{u}{u_0} = -\frac{avw}{b}\,.\,\frac{x_0 - x}{x_0 x},$$

which may be written

$$-\log \frac{u}{u_0} = \frac{avw}{bx_0 \log_e 10}\,.\,\frac{x_0 - x}{x} = A\,.\,\frac{x_0 - x}{x}. \tag{4}$$

This equation represents any one reaction of the kind specified during the concentration required in an ordinary estimation of albuminoid ammonia, but the mathematical expression must not be pressed too far. Thus, if we make $x = 0$, this not only implies that the contents of the retort are evaporated to dryness, but also that the reagents have gained infinite concentration, and therefore act with resistless force, effecting complete alteration of any remaining traces of the nitrogenous body. The form of the curve varies greatly with the value of A. Two examples are given in the figure. Curve B represents this equation when $A = 1$; curve C when $A = \frac{1}{10}$. Since the quantity of ammonia present at any moment (both in retort and distillate) is proportional to the weight of the nitrogenous body transformed, we may write

$$u_0 - u : u_0 :: (y + z) : (y + z)_\infty,$$

where subscript ∞ is used to denote the ultimate value theoretically possible; or, in another form (since $y_\infty = 0$),

$$\frac{u}{u_0} = \frac{z_\infty - (y + z)}{z_\infty}. \qquad (5)$$

The curves B and C are so drawn that ordinates represent $(y + z)$ as a function of x.

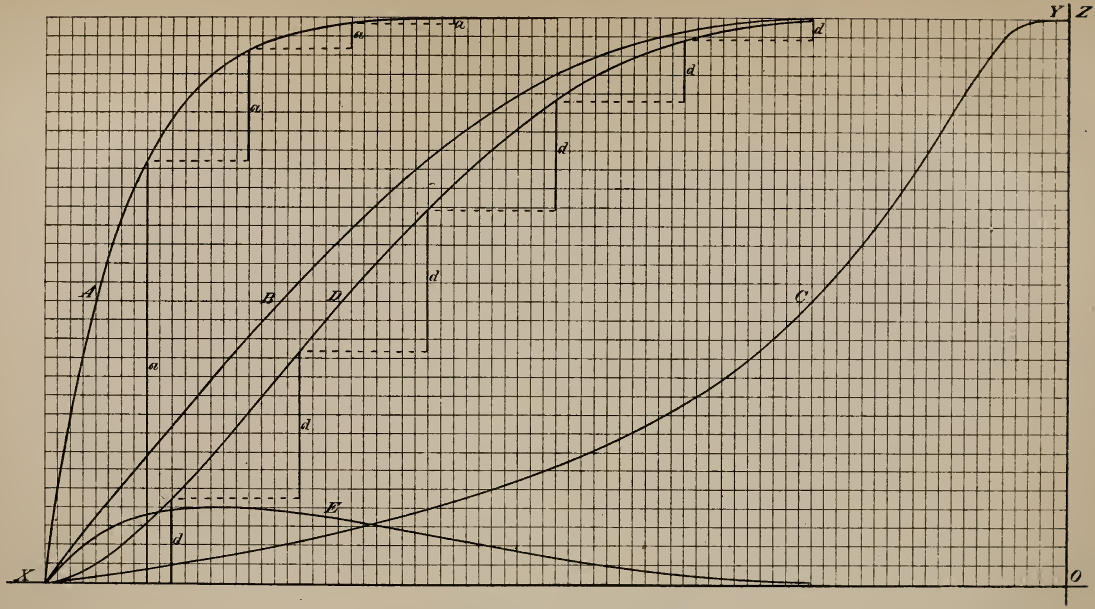
It will be seen at once that when $A = 1$ the quantity of ammonia increases very rapidly during the first part of the distillation, but when $A = 0.1$, $(y + z)$ increases but slowly until the fluid is considerably concentrated. Equation (4) suggests various modifications by which A may be altered at pleasure; for example, by increasing the quantity of permanganate used (represented by w), or by distilling a less quantity (b) each minute. Thus Smart noted several instances of increased action by slower boiling.

Curves of similar properties express the progress of other reactions which take place during concentration in large excess of reagents. Equations of the following forms are obtained by varying the exponent of x in equation (3) and using the appropriate constants. For reactions involving the concurrence of two molecules only,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = -A . \log \frac{x}{x_0}. \qquad (6)$$

For three molecules,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = A \frac{x_0 - x}{x}. \qquad (7)$$



EXPLANATION OF THE FIGURE.

A. Curve of distillation of free ammonia. *a*, *a*, *a*. Fractions, each $\frac{1}{10}$ the original volume. *B*. Formation of albuminoid ammonia, eq. (7); $A = 1$. *C*. Formation of albuminoid ammonia, eq. (7); $A = \frac{1}{10}$. *D*. Ammonia in distillate, from curve *B*. *d*, *d*, *d*. Fractions, each $\frac{1}{8}$ the original volume. *E*. Ammonia in retort, from curve *B*. Values of x, although positive, are measured towards the *left*, in order that time may be counted towards the *right*.

For four molecules,

$$-\log \frac{z_\infty - (y+z)}{z_\infty} = A \frac{x_0^2 - x^2}{x^2}. \tag{8}$$

In all such cases the formation of ammonia may take place most rapidly in the early, middle or latter part of the distillation, according to the value of A.

If the ammonia, instead of appearing directly, is the final product of a succession of different reactions, a complete theory must take account of the gradual formation and disappearance of the intermediate products. Some evidence on this point will appear in section VI.

IV. *Distillation of Albuminoid Ammonia.*

Equation (1) applies to the distillation of ammonia only when the total quantity $(y+z)$ remains constant; otherwise we must write $-dz$ in place of dy. Thus,

$$\frac{-dz}{dx} = k \cdot \frac{y}{x}, \tag{9}$$

or

$$y = -\frac{x}{k} \cdot \frac{dz}{dx}. \tag{10}$$

Substituting in equation (7),

$$-\log\left(1 + \frac{xdz}{kz_\infty dx} - \frac{z}{z_\infty}\right) = A \frac{x_0 - x}{x}. \tag{11}$$

This equation (as soon as a fixed value is given to A) expresses a perfectly definite relation between the ammonia distilled and the volume remaining in the retort. It is not easy, however, to obtain an integral in form suitable for computation, and an indirect method was used. The ordinates of curve B represent the sum of y and z when $A=1$; these ordinates were divided into two parts, in accordance with the condition implied in equation (9). Curve D thus represents the gradual increase of z, and curve E shows the increase and subsequent decrease of y. A few corresponding points of these three curves are also indicated in the following table, increments of z being placed under the symbol Δz. These increments are shown on the figure as *d*, *d*, *d*. For convenience, z_∞ is taken as unit of weight for ammonia, and x_0 is made equal to 8; as when a volume of 400 cc. is distilled in fractions of 50 cc. each. The ratio of each increment to the next is stated under r.

x.	$y+z$.	y.	z.	Δz.	r.
8	.000	.000	.000	...	...
7	.280	.129	.151	.151	.58
6	.535	.122	.413	.262	1.05
5	.749	.087	.662	.249	1.31
4	.900	.047	.853	.191	1.74
3	.978	.015	.963	.110	3.23
2	.999	.002	.997	.034	...
0	1.000	.000	1.000	...	...

When $A = 1$ (as in this table), y reaches a maximum when $x = 6.7$, during the collection of the second fraction of distillate; and this fraction contains the largest quantity of ammonia. The third fraction contains nearly the same amount, but later increments show a rapid decrease. The large increase of ammonia indicated for the second measure is due in very small part to the increased concentration of the permanganate, but chiefly to the fact that sufficient time has elapsed for the accumulation of ammonia in the retort. An increase in the second measure has been rarely observed in practice, except in a few experiments on pure chemicals, such as urea, theine, glychocholic acid, and notably in cyanuric acid. In the 59 samples of natural waters already referred to, the first measure always contained as much as $1\frac{1}{3}$ times that found in the second; in 11 instances the ratio is 2, and in 33 instances it is more than 2. On the other hand, instead of an increase in this ratio for succeeding portions (as indicated by theory for a single reaction), it usually decreases, the ratio of the last two determinations being from 1 to 2. This want of agreement between the theory for a single reaction and observations on a natural water are exactly what we should expect; for the water may contain a great number of different substances, each undergoing change according to equation (6), (7) or (8), so that the actual rate of distillation depends upon the sum of the ammonia derived from all these sources. As curve E shows a rapid rise from zero to a maximum, followed by a gradual decrease to zero, so we may conceive a multitude of similar curves, with their several maxima at various points, but with a large share of them near the origin; implying $A > 1$, for the most part. The resultant of all such curves might have a single maximum, like the type given, or it might have a succession of maxima and minima. On the theory of averages, the former seems more probable. This resultant curve might have a great variety of form in details, answering to the various behavior of different waters.

V. *Exterpolation Formula for Residue in Retort.*

Many chemists, feeling that the task is not completed by nesslerising three measures, have pushed the distillation much farther. Mallet[1] suggests a certain limit as criterion when the distillation has been carried far enough. If the ammonia found in the successive portions is reported, we can rudely plat the curves for ammonia distilled, ammonia in retort, or total ammonia formed. Each of these curves may be the resultant of many similar curves having different parameters. Can we find an empirical equation for the resultant that will conform to the analytical results, and thus enable us to apply a probable correction for the ammonia that would be obtained if the distillation were completed?

We may assume a curve of the form

$$y = Ax + Bx^2 \qquad (12)$$

to indicate the varying quantity of ammonia in the retort under the condition that this is all distilled away when the fluid is gone. Substituting in equation (9),

$$\frac{-dz}{dx} = kA + kBx.$$

Integrating between the limits z_1 and z_2,

$$z_2 - z_1 = kA\,(x_1 - x_2) + \tfrac{1}{2}kB\,(x_1^2 - x_2^2)\,;$$

or, for brevity,

$$\Delta_1 z = kA\Delta_1 x + \tfrac{1}{2}kB\Delta_1 x^2. \qquad (13)$$

In like manner, for a second increment of z and for the undetermined portion,

$$\Delta_2 z = kA\Delta_2 x + \tfrac{1}{2}kB\Delta_2 x^2,$$

$$\Delta_\infty z = kA\Delta_\infty x + \tfrac{1}{2}kB\Delta_\infty x^2. \qquad (14)$$

Those who follow Wanklyn's directions for 500 cc. of water begin the distillation of albuminoid ammonia with 350 cc. of fluid, and distill three measures of 50 cc. each, rejecting the last 200 cc. Taking 50 cc. as unit of volume, $x_1 = 6$, $x_2 = 5$, and $x_3 = 4$, while $\Delta_1 z$ and $\Delta_2 z$ represent the ammonia found in the second and third measures. Assume $\Delta_1 z = r\Delta_2 z$, then

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[1] *Loc. cit.* p. 208.

$$r\Delta_2 z = kA\,(6-5) + \tfrac{1}{2}kB\,(36-25) = kA + 5.5kB\,,$$
$$\Delta_2 z = kA\,(5-4) + \tfrac{1}{2}kB\,(25-16) = kA + 4.5kB\,.$$

By elimination,

$$kB = (r-1)\,\Delta_2 z \text{ and } kA = (5.5-4.5r)\,\Delta_2 z\,.$$

But

$$\Delta_\infty z = 4kA + 8kB\,,$$
$$\therefore\quad \Delta_\infty z \doteq (14-10r)\,\Delta_2 z\,. \qquad (15)$$

If

$$r = 1\,,\ \Delta_\infty z = 4\Delta_2 z\,;$$

that is, if the second and third measures yield like quantities of ammonia, the best correction we can make is to assume that the distillation of four times 50 cc. still remaining in the retort would yield four times that quantity.

If $r > 1\frac{2}{9}$, the value of A becomes negative, and therefore y becomes negative for small values of x. This involves a physical impossibility, but we may meet the difficulty by treating the equation

$$y = Ax^2 + Bx^3 \qquad (16)$$

in the same manner as equation (13), whence

$$\Delta_\infty z = \frac{188-100r}{37}\,\Delta_2 z\,, \qquad (17)$$

a correction which again fails if $r > \frac{91}{61}$.[1]

We may test these formulas by means of Smart's experiments with pure chemicals; but, as he began the action with 400 cc. of fluid instead of 350, $\Delta_1 z$ and $\Delta_2 z$ represent his third and fourth fractions, with the advantage of greater distance from the beginning of the operation, where equation (12) is wholly inapplicable. The available data (for values of r between 1 and 1.5) are given in the following table, which states under

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[1] To obtain a more general formula for the correction proposed, we may assume

$$y = Ax^n + Bx^{n+1}\,, \qquad (18)$$

whence, by the same treatment illustrated above,

$$\Delta_\infty z = \frac{(\Delta_1 x^{n+1} - r\Delta_2 x^{n+1})\,\Delta_\infty x^n - (\Delta_1 x^n - r\Delta_2 x^n)\,\Delta_\infty x^{n+1}}{\Delta_2 x^n \Delta_1 x^{n+1} - \Delta_1 x^n \Delta_2 x^{n+1}}\,\Delta_2 z\,, \qquad (19)$$

where A is positive or zero when

$$r \leqq \frac{\Delta_1 x^{n+1}}{\Delta_2 x^{n+1}}\,. \qquad (20)$$

We may either make n the smallest integer consistent with the condition (20), or we may determine n by making the fraction equal to r. The function $\Delta_\infty z = \phi(r)$ will be a smooth curve in either case, consistent with the theory as developed above and with the analytical results.

A, per cent. ammonia found in the first four fractions;
B, per cent. ammonia found in "exhaustive experiments";
C, per cent. ammonia obtainable after the first four fractions; and
D, per cent. ammonia indicated by the exterpolation formulas.

	A.	B.	C.	D.
Silver and potassium cyanide, .	2.25	[17.1]	14.85	2.4
Prussian blue, ...	.3	25.8	25.5	.2
Urea, from urine, ...	8.7	43.10	34.4	8.8
	8.65	...	34.45	6.6
Urea, from ammonium cyanate, .	7.7	43.4	35.7	8.0
	7.5	...	35.9	8.0
Alloxan, ...	6.55	21.3	14.75	2.5
	6.6	...	14.7	2.4
Thiocarbanilide, ...	4.15	11.85	7.7	1.6
Thiocarbamide, ...	15.25	22.50	7.25	1.7
	15.0	...	7.5	1.6
Strychnine sulphate, ...	4.0	5.4	1.4	.4
	3.75	...	1.65	1.0
Codeine, ...	5.0	5.32	.32	.5

A glance at the last two columns shows that the ammonia actually obtainable after one-half the fluid had been distilled was many times the proposed correction. An explanation of this discrepancy will next be considered.

VI. *Evidence of Intermediate Compounds of Nitrogen.*

Making some allowance for the difference between equation (7) (which was selected for study) and equations (6) and (8), it is safe to conclude from the table in section IV, that if the action of alkaline permanganate upon a pure compound of nitrogen could be represented by any single chemical equation (no matter how complex), we should have reason to expect this change to take place with such speed that fully 70 per cent. of the theoretical yield of ammonia would be obtained by distilling one-half the fluid, or else with such slowness that the first measure would contain far less ammonia than the second. Published experiments with at least eight bodies[1] contradict both these conditions, and we are forced to believe that in the earlier stages some molecules of the original body yield ammonia with promptness, while others are converted into more stable forms and resist the action with great stubbornness. The nature of these intermediate products is not yet clear, except only that *a* (as defined in section III) is small, in their reaction with alkaline permanganate. Perhaps they may be chiefly condensation products. Alloxan, which yielded 4 per cent. ammonia in the first fraction (eighth) of distillate, and only 2.57 per cent. in the next three, but 21.3 per cent. by prolonged action, is a marked example of such behavior; this, no doubt, is partly converted into parabanic acid. So, likewise, in a water analysis, many substances may yield a small part of their nitrogen as ammonia, while the greater part is converted into more stable forms which elude detection. It has been supposed that the organic matter of potable water is more like asparagine, yielding its nitrogen readily under the action of permanganate. Of this, however, I have found no proof. In about 40 per cent. of the natural potable waters referred to, the ratio of the third and fourth fractions is 1.5 or less, giving grave suspicion of incompleted action when the distillation was stopped. Even if the yield of ammonia in some fraction has fallen below the limit of delicacy in nesslerising, what evidence have we that prolonged treatment would not develop a much larger amount of ammonia than that already obtained?

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[1] These are the first six named in the last table, besides parabanic acid and theine.

VII. *Applications to the Analytical Process.*

A debt of gratitude is due to Professor J. Alfred Wanklyn, as the author of a valuable method of analysis which has done much in the interest of public health. "The ammonia process," which originated in 1867, is still described in the 7th edition of "Water Analysis" (1889) essentially as in the author's first paper upon the subject. In a process of such delicacy, where the results may be influenced by a multitude of variable conditions, it is desirable that these should be accurately defined and conscientiously followed. According to the author's latest directions, 500 cc. of water are reduced to 300 cc. (to remove free ammonia) and 50 cc. of the reagent added; three measures of distillate are then collected, when "the distillation may be stopped. . . . It is necessary to nesslerise each separate 50 cc. of distillate, and to add the amounts together, in order to arrive at the total albuminoid ammonia." Besides this process, a second is described upon a scale of one-fifth, with this important modification, that the operation is "continued so long as 10 cc. of distillate shows a sign of ammonia"; if, then, with a delicate Nessler reagent, ammonia is found in the sixth measure of distillate, the fluid must be evaporated to dryness!

But why should 350 cc. be distilled until only $\frac{3}{7}$ have gone over, while 70 cc. are distilled up to a very different limit? Probably because the *time* required to evaporate 30 cc. from the smaller retort proved insufficient for both the chemical action required and for the separation of the ammonia. Professor Wanklyn's method, as conducted in his own laboratory and by his own hands, has doubtless done valuable service, yielding good comparable results; but more definite conditions must be adopted if we would avoid discrepancies among different places and persons. Its value depends upon giving constant and comparable results under fixed conditions. For the absolute estimation of organic nitrogen, it is worthless.

It will be instructive to divide the free or albuminoid ammonia found in each measure of distillate by that found in the next, and to record the ratio so found; especially if care is taken to boil at a constant rate. According to Smart,[1] with pure animal or vegetable albuminoids, $r = 2$; but if these have passed into the putrefactive condition, $r = 3$; while in the case of urea (after the preliminary stage is passed) $r = 1$, both for free and for albuminoid ammonia. The successful detection of recent sewage is reported, when the chemical evidence consisted in the persistent evolution of free ammonia, followed by persistent evolution of twice as much albuminoid ammonia.

The term "albuminoid ammonia," like "reverted phosphoric acid," has a technical significance determined by the method adopted in the analysis. The actual market value of reverted phosphoric acid cannot be so high under the rule for extraction at 65° as under the rule for extraction at 40°; so also 0.1 mgm. of ammonia obtained by prolonged and intense action is of less real importance than the same quantity obtained by less vigorous measures. Many modifications of the original process have been proposed; among these Breneman's[2] are worthy of special consideration. If the fluid is brought nearly to dryness, as he suggests, it may be possible to apply an exterpolation formula, such as equation (19), to the measured residue. The detailed record of ammonia found in seven successive fractions (with greatly increased temperature and concentration at the last) may help to distinguish between different kinds of nitrogenous matter, yielding ammonia more readily and less readily; but care should be used in regard to the volume of the residue; if this is 4 cc. in one case and 7 cc. in another, there may be considerable difference in the oxidation of that comparatively inert matter which we have been led to suspect.

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[1] Public Health (Minn.), Vol. II, No. 3, May, 1886.

[2] Jour. Amer. Chem. Soc. 8, No. 9.

If the ammonia process should be applied to investigations of the relative stability of organic compounds,[1] the formulas given above may be adapted to numerous possible modifications. The use of return-flow condenser (to prolong the chemical action apart from distillation), and variations in the proportions of potash and permanganate, do not seem to have yet been tried. It is difficult to see why the alkali should always be used in so much greater excess than the oxidiser (in spite of inconvenient bumping), but it is especially strange that the distinguished author, ignoring Mallet's report of 1882, and republishing his directions without any revision, should leave the important question of *time* entirely out of account. "Suffering persecution for the sake of the truth" should make the scientist keenly alive to any truthful criticism, and ready to study the contributions of his colleagues. The "ammonia process" has now passed from one laboratory into a hundred. If "discovered about a generation before chemists were prepared for it," the time is now fully ripe to collect the testimony of those who have used it; to agree upon the general conditions of quantity, rate of boiling, and limit of distillation, and even upon such details as the matter of paper or rubber connections. When a satisfactory compromise is effected we may hope to have a uniform method of procedure and a real definition of albuminoid ammonia.

WASHINGTON, D. C., *August*, 1889.

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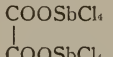
[1] It may be of interest to compare such results with those of Dreyfus, who studied the rate of oxidation with acid solution of permanganate. Compt. rend. **105**, 523.

ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON PHENOL.[1]

BY RICHARD ANSCHÜTZ AND WILLIAM O. EMERY.

Evans and one of us[2] have recently shown that the first product of the action of antimony pentachloride on anhydrous oxalic acid very probably has the constitution



$$\begin{array}{l} COOSbCl_4 \\ | \\ COOSbCl_4, \end{array}$$

and further, that antimony pentachloride is not decomposed by water, but rather unites with water.

The results of these investigations have disclosed to us the fundamental difference in the behavior of antimony pentachloride and phosphorus pentachloride, not only towards water, but also towards carbon compounds which contain oxygen and hydrogen.

On the other hand, phosphorus pentachloride behaves like antimony pentachloride, inasmuch as it substitutes chlorine for hydrogen in those organic compounds which contain no oxygen,[3] or oxygen in such firm combination with carbon as not to be available for the formation of phosphorus oxychloride.[4]

The compound $(COOSbCl_4)_2$ is of special interest as indicating the manner in which phosphorus pentachloride acts on substances containing the hydroxyl group. The first phase of the reaction evidently consists in the formation of compounds of analogous constitution. If the oxygen of the hydroxyl group is easy of substitution, phosphorus oxychloride is formed. If, on the other hand, the oxygen is difficult of elimination, as in the case of phenols and hydroxy acids, it might be possible to prepare substances which are constituted according to the general formulae,

$$R.O.PCl_4,\ (R.O)_2PCl_3 \text{ and } (R.O)_3PCl_2.$$

Considerations like the above have led us to attempt the preparation of the phenoxyl derivatives of phosphorus pentachloride. In the belief that these substances could be more easily prepared by an indirect method than by direct substitution of one, two or three chlorine atoms in phosphorus pentachloride with phenoxyl rests, we have first prepared the phenoxyl derivatives of the trichloride and then treated these with chlorine.

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[1] For the analytical details see the original articles in the Annalen der Chemie.

[2] Ann. Chem. (Liebig) **239**, 285.

[3] Compare for example Albert Colson and Henri Gautier, Compt. rend. **101**, 1064.

[4] Ann. Chem. (Liebig) **239**, 297.

As E. Noack[1] has shown, the following substances are formed by the action of phosphorus trichloride on phenol:

Phenyl-phosphorous dichloride,	$C_6H_5OPCl_2$.
Diphenyl-phosphorous monochloride,	$(C_6H_5O)_2PCl$.
Phosphorous triphenylester,	$(C_6H_5O)_3P$.

The difficulties which Noack encountered in separating these substances become unimportant if the product of the reaction be rectified under greatly diminished pressure.

Phenyl-phosphorous dichloride, $C_6H_5OPCl_2$, is a colorless, highly refractive liquid, smells strongly of hydrochloric acid, and is readily decomposed by water into phenol, phosphorous and hydrochloric acids. It is easily soluble in ether, chloroform, carbon tetrachloride, and benzene, and boils under a pressure of 11 mm. at 90° (temperature of paraffin-bath 110°).

The specific gravity, determined by means of a Sprengel's pyknometer, was found to be

$$d\frac{20}{4} = 1.35422.$$

Diphenyl-phosphorous monochloride, $(C_6H_5O)_2PCl$, is obtained as a by-product in the preparation of the chloride $C_6H_5OPCl_2$. It is a colorless, very refractive liquid, decomposes readily in presence of moisture, and boils at 172° (temperature of paraffin-bath 190°) under a pressure of 11 mm.

The specific gravity was found to be

$$d\frac{20}{4} = 1.24378.$$

Phosphorous triphenylester, $(C_6H_5O)_3P$, occurs as by-product in the preparation of the two preceding chlorides; is formed exclusively by the action of three molecules of phenol on one molecule of phosphorus trichloride. The ester boils under a pressure of 11 mm. at 220°. On one occasion it was obtained as a snowy-white crystalline solid. In this condition it remained some time, but finally assumed the liquid state again.

The specific gravity we found to be

$$d\frac{20}{4} = 1.18428.$$

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[1] Ann. Chem. (Liebig) **218**, 85.

Action of Phosphorus Pentachloride on the Phenoxyl Derivatives of Phosphorus Trichloride.

Having investigated the phenoxyl derivatives of the trichloride, we next attempted the preparation of the compounds

$$C_6H_5OPCl_4,$$
$$(C_6H_5O)_2PCl_3,$$
$$(C_6H_5O)_3PCl_2,$$

according to the equations

$$C_6H_5OPCl_2 + PCl_5 = C_6H_5OPCl_4 + PCl_3,$$
$$(C_6H_5O)_2PCl + PCl_5 = (C_6H_5O)_2PCl_3 + PCl_3,$$
$$(C_6H_5O)_3P + PCl_5 = (C_6H_5O)_3PCl_2 + PCl_3.$$

Apparently no action takes place in the cold when the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, $(C_6H_5O)_3P$ are mixed with phosphorus pentachloride. If, however, any one of them be heated with the pentachloride in molecular proportions to 100° in sealed tubes, a crystalline compound, soluble in chloroform and carbon tetrachloride, is formed.

The course of the reaction of phosphorus pentachloride on phenyl-phosphorous dichloride was very interesting. Upon heating the two substances, the pentachloride gradually disappeared; the new compound could be seen as minute oily globules, swimming about in the phosphorus trichloride, and finally the whole was found to consist of two distinct layers, one of which solidified on cooling. The liquid part boiled at 78° and was identified as phosphorus trichloride. Although the formation of phosphorus trichloride may be regarded as an indirect proof that the crystalline substance was the tetrachloride, $C_6H_5OPCl_4$, nevertheless we were unable by this method to isolate this substance in a pure condition.

We have further observed the formation of phosphorus trichloride by the action of the pentachloride on the substances $(C_6H_5O)_2PCl$ and $(C_6H_5O)_3P$, but we have not been able to separate the addition products in pure condition.

Action of Chlorine on the Phenoxyl Derivatives of Phosphorus Trichloride.

Since we were unable to prepare the phenoxyl addition-products of the trichloride by the action of phosphorus pentachloride on the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, $(C_6H_5O)_3P$, we attempted their preparation by the action of free chlorine. The simplest reaction possible in the case of the chloride, $C_6H_6OPCl_2$, may be represented by the equation

$$C_6H_6OPCl_2 + Cl_2 = C_6H_6OPCl_4,$$

analogous to the behavior of phosphenyl chloride towards chlorine,

$$C_6H_5PCl_2 + Cl_2 = C_6H_6PCl_4;$$

and experiment has, indeed, demonstrated that the reaction does take place in the manner indicated. Owing to the extreme readiness, however, with which these addition products are decomposed by even traces of moisture, it was some time before we discovered a suitable method of purifying them.

We operated as follows: Phenyl-phosphorous dichloride, $C_6H_6OPCl_2$, was dissolved in dry ether, and a stream of dry chlorine was conducted over the surface of the solution. The chlorine was absorbed with great avidity. So much heat was generated during the operation that we considered it advisable to cool the mixture. The new compound separated as colorless crystalline leaflets. We continued to treat the ethereal solution with chlorine till the mass had assumed a faint yellow color, due to excess of chlorine. The crystals were first freed from the mother-liquor by decantation, then washed with dry ether. As the new compound is extremely hygroscopic, we were obliged to exercise the utmost care and expedition in weighing and preparing it for analysis.

Phenyl-phosphoric tetrachloride, $C_6H_5OPCl_4$, crystallises in small colorless leaves which are soluble in chloroform and carbon tetrachloride, insoluble in ether and petroleum ether. It deliquesces to an oily mass in the air. On treatment with water it decomposed violently. The aqueous solution, which contained phosphoric and hydrochloric acids, was extracted with ether and the ethereal solution rectified under diminished pressure. A comparatively small portion distilled under a pressure of 11 mm. at 245°. The distillate soon solidified to a brownish crystalline mass. Upon recrystallising from alcohol, colorless needles, fusing at 44°-45°, were obtained. Analysis showed them to have the composition $(C_6H_5O)_3PO$.

Michaelis[1] has shown that phosphenyl tetrachloride and sulphur dioxide yield phosphenyl oxychloride and thionyl chloride, according to the equation

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[1] Ann. Chem. (Liebig) 181, 297.

$$C_6H_5PCl_4 + SO_2 = C_6H_5POCl_2 + SOCl_2.$$

We thought it of interest to ascertain the behavior of our chloride under like conditions. Upon treating the tetrachloride with sulphur dioxide and rectifying, we obtained two fractions, the first of which boiled at 78° (thionyl chloride), the second at 121°–122°, under a pressure of 11 mm. Analysis proved it to have the composition $C_6H_5OPOCl_2$. The reaction may, therefore, be expressed by the equation

$$C_6H_5OPCl_4 + SO_2 = C_6H_5OPOCl_2 + SOCl_2.$$

Diphenyl-phosphoric trichloride, $(C_6H_5O)_2PCl_3$, was prepared by treating a dry ethereal solution of the monochloride, $(C_6H_5O)_2PCl$, with chlorine. The addition product separated as a yellow oil, which gradually solidified to minute crystals. These were purified by washing with ether, and were dried in a desiccator. The trichloride is soluble in chloroform, insoluble in ether, and decomposes easily on heating. Upon treatment with water, extraction of the aqueous solution with ether and rectification in a vacuum, a fraction, boiling at 245° under a pressure of 11 mm., was obtained. This recrystallised from alcohol, fused at 44°–45°, and was found to consist of triphenyl phosphate, $(C_6H_5O)_3PO$.

We are unable to decide whether the formation of this ester in the above mentioned cases takes place in aqueous solution, or whether it is formed by heating the product of the reaction at 245° under a pressure of 11 mm.

Triphenyl-phosphoric dichloride, $(C_6H_5O)_3PCl_2$.—The formation of this compound is perfectly analogous to that of the tetrachloride, $C_6H_5OPCl_4$. We have obtained it but once as a crystalline solid. In most cases it only solidified in a freezing mixture of ether and carbonic acid. Water decomposes it into triphenyl phosphate and hydrochloric acid.

It is evident that these three addition-products,

$$\begin{gathered} C_6H_5OPCl_4, \\ (C_6H_5O)_2PCl_3, \\ (C_6H_5O)_3PCl_2, \end{gathered}$$

are formed by the direct action of phosphorus pentachloride on phenol, analogous to the formation of the compounds

$C_6H_5OPCl_2$,
$(C_6H_5O)_2PCl$,
$(C_6H_5O)_3P$,

by the action of phosphorus trichloride on phenol. But, while these last can be easily separated and purified by rectification under diminished pressure, their chlorine addition-products are solids, which are decomposed even under diminished pressure, and further, are so hygroscopic that a separation and purification by fractional crystallisation was entirely out of the question.

Action of Bromine on the Phenoxyl Derivatives of Phosphorus Trichloride.

Although the behavior of bromine as compared with that of chlorine seemed of minor importance, we have nevertheless prepared the compounds $C_6H_5OPCl_2Br_2$ and $(C_6H_5O)_2PClBr_2$.

As is known, phosphorus trichloride yields the compound PCl_3Br_2 with great difficulty, and only in the cold. Michaelis[1] has shown that if a chlorine atom of the trichloride be replaced by the phenyl group, the tendency of phosphorus to unite with bromine is increased. It was, therefore, of interest to learn whether the phenoxyl group would produce a like effect.

Phenyl-phosphoric dichloride dibromide, $C_6H_5OPCl_2Br_2$, was prepared by treating the ethereal solution of the chloride, $C_6H_5OPCl_2$, with the dry vapor of bromine. The new compound separated as a reddish oil, which soon solidified to a yellow crystalline mass. It was purified by washing with ether. This addition product is exceedingly unstable, being readily decomposed by moisture or even when kept in sealed tubes.

Diphenyl-phosphoric monochloride dibromide, $(C_6H_5O)_2PClBr_2$. The method of preparation is perfectly analogous to that of the preceding compound, and it is equally unstable.

Action of Sulphur on the Phenoxyl Derivatives of Phosphorus Trichloride.

In our investigations we have further studied the behavior of the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, and $(C_6H_5O)_3P$ towards sulphur. Experiment has shown that phosphorus trichloride unites with sulphur only when heated in sealed tubes at 130°. We have found that a higher temperature is necessary to bring about the reaction if the chlorine of the trichloride be replaced by one or more phenoxyl groups.

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[1] Ann. Chem. (Liebig) **181**, 298.

Phenyl-thiophosphoric dichloride, $C_6H_5OPSCl_2$, was made by heating equal molecular weights of the chloride, $C_6H_5OPCl_2$, and sulphur a short time at 190°. The reaction appears to begin at about 160°; is not complete, however, below 190°. The compound is formed according to the equation

$$C_6H_5OPCl_2 + S = C_6H_5OPSCl_2.$$

The product was purified by rectifying under diminished pressure. The new compound boiled at 119°–120° (temperature of paraffin-bath 140°) under a pressure of 11 mm., and had a specific gravity,

$$d\tfrac{20}{4} = 1.40593.$$

It is a colorless, highly refractive liquid, easily soluble in ether and chloroform.

We endeavored to prepare the compounds $C_6H_5OPSCl_2$ and $(C_6H_5O)_2PSCl$ by the action of phosphorus thiochloride on phenol, according to the equations

$$C_6H_5OH + PSCl_3 = C_6H_5OPSCl_2 + HCl,$$
$$2C_6H_5OH + PSCl_3 = (C_6H_5O)_2PSCl + 2HCl,$$

analogous to the action of phosphorus oxychloride on phenol:

$$C_6H_5OH + POCl_3 = C_6H_5OPOCl_2 + HCl,$$
$$2C_6H_5OH + POCl_3 = (C_6H_5O)_2POCl + 2HCl.$$

A mixture of phenol and phosphorus thiochloride was heated to 170° till evolution of hydrochloric acid had ceased. Upon rectifying the product, we were unable to detect even traces of the compounds $C_6H_5OPSCl_2$ and $(C_6H_5O)_2PSCl$. The neutral ester of thiophosphoric acid seemed to be the only product of this reaction.

From this we conclude that the dichloride, $C_6H_5OPSCl_2$, as well as the monochloride, $(C_6H_5O)_2PSCl$, have a greater tendency to react with phenol than phosphorus thiochloride, according to the equations

$$C_6H_5OPSCl_2 + 2C_6H_5OH = (C_6H_5O)_3PS + 2HCl,$$
$$(C_5H_6O)_2PSCl + C_6H_5OH = (C_6H_5O)_3PS + HCl.$$

Diphenyl-thiophosphoric monochloride, $(C_6H_5O)_2PSCl$, was prepared by heating molecular weights of the chloride, $(C_6H_5O)_2PCl$, and sulphur a short time at 190°. The product, purified by distillation, had a melting point of 63°–64°, and a boiling point of 194° under a pressure of 11 mm.

Triphenyl-thiophosphate, $(C_6H_5O)_3PS$, we obtained by heating molecular weights of the ester, $(C_6H_5O)_3P$, and sulphur at 190°. It crystallises in needles, which melt at 49°–50°, and boil at 245° under a pressure of 11 mm. The specific gravity was found to be

$$d\frac{20}{4} = 1.24411.$$

This ester was first obtained by Schwarze,[1] by the action of phosphorus sulphochloride on phenol. We have repeated his experiments and can corroborate his statements.

The striking similarity of triphenyl phosphate, $(C_6H_5O)_3PO$, to triphenyl thiophosphate, $(C_6H_5O)_3PS$, in melting and boiling points led us to compare the first products of the action of phosphorus oxychloride and phosphorus thiochloride on phenol. We prepared the compounds $C_6H_5OPOCl_2$ and $(C_6H_5O)_2POCl$ according to the directions of Jacobsen,[2] and rectified them under diminished pressure. The following table renders easy a comparison of the substances in question:

Formula.	Boiling Point.	Spec. Grav. and Melt. Pt.
$C_6H_5OPOCl_2$	116°–117° by 13–14 mm. pressure	$d\frac{20}{4} = 1.41214$
$C_6H_5OPSCl_2$	119 –120 " 11 " "	$d\frac{20}{4} = 1.40593$
$(C_6H_5O)_2POCl$	195 " 13–14 " "	$d\frac{20}{4} = 1.29604$
$(C_6H_5O)_2PSCl$	194 " 11 " "	Melt. pt. 63°–64°
$(C_6H_5O)_3PO$	245 " " " "	" 45
$(C_6H_5O)_3PS$	245 " " " "	" 49 –50

It will be readily seen from the above that the introduction of a sulphur atom in place of a corresponding oxygen atom in the chloride, $C_6H_5OPOCl_2$, causes but a slight raising of the boiling point as well as but a slight decrease in the specific gravity. Diphenyl-phosphoric monochloride and diphenyl thiophosphoric monochloride have very nearly the same boiling points under the same pressure. The former is, however, a liquid, while the latter is a solid. Triphenyl phosphate and triphenyl thiophosphate have identical boiling points under the same pressure, and the melting points lie but 4° apart.

The change in the properties, brought about by the introduction of a sulphur atom in place of a corresponding oxygen atom, appears to be the smaller, the larger the molecule of the organic compound in which the change occurs.

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[1] Ann. Chem. (Liebig) **127**, 157.

[2] Ber. d. chem. Ges. **8**, 1521.

Of the new compounds described in this paper, the tetrachloride, $C_6H_5OPCl_4$, seemed to possess the greatest theoretical interest. Although we have thus far been unable to prove it to be the first product of the action of phosphorus pentachloride on phenol, and were only able to prepare it by an indirect method, still we do not for a moment doubt that it is the first product in the above mentioned reaction.

If we assume the compound $C_6H_5OPCl_4$ to be the first product of the action of phosphorus pentachloride on phenol, then this reaction speaks very strongly in favor of the pentavalence of phosphorus in phosphorus pentachloride.

The existence of this compound $C_6H_5OPCl_4$ affords an entirely new view of the manner in which phosphorus pentachloride acts on all hydroxyl compounds. We may assume that the first phase of such a reaction consists in the formation of substances constituted according to the general formula,

$$R'OPCl_4.$$

If the oxygen atom be loosely bound to the radical R′, the second phase of the reaction would consist in the substitution of chlorine for oxygen and the formation of phosphorus oxychloride.

ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON SALICYLIC ACID.[1]

By Richard Anschütz and William O. Emery.

After the investigations of Moore and one of us[2] had to a certain extent explained the manner in which phosphorus pentachloride reacts with salicylic acid, it seemed to be of particular interest to study the behavior of phosphorus trichloride towards this acid. As has been shown, the pentachloride acts not only on the phenol- but also on the carboxyl-hydroxyl. We could not with certainty predict how the trichloride would behave towards salicylic acid, and indeed a very remarkable substance results, the formation of which will be described below. Several preliminary

[1] For the analytical details see original articles in the Annalen der Chemie.

[2] Ann. Chem. (Liebig) **228**, 308; **239**, 314. This Journal **10**, 296.

experiments had shown that salicylic acid reacts with phosphorus trichloride, and that the first product, obtained by the employment of equivalent molecular weights, can be isolated; that, however, the yield of the new compound may be essentially increased if an excess of the trichloride be employed. Phosphorus trichloride and salicylic acid do not apparently react in the cold. No hydrochloric acid is given off in any appreciable quantity before the paraffin-bath, in which the mixture is heated, has attained a temperature of 70°. We operated as follows: 50 grams of freshly distilled phosphorus trichloride and 24 grams of absolutely dry salicylic acid were brought into a distilling flask connected with an inverted condenser, and the mixture gradually heated to 70°. The escaping hydrochloric acid was conducted into a weighed flask containing water. The rate of evolution could be easily regulated by raising or lowering the temperature of the bath. After heating two hours, the reaction was practically at an end, though minute quantities of gas continued to be given off on longer heating. We have found that the largest yield of the new compound is obtained by keeping the temperature between 70° and 85°. We rectified the colorless product of the reaction first under ordinary pressure, whereby the excess of phosphorus trichloride was separated, then under greatly reduced pressure. The new product distilled under a pressure of 11 mm. at 127° (temperature of paraffin-bath 150°), and soon solidified to beautiful transparent crystals in the well cooled receiver. Analysis as well as the quantitative course of the reaction established the formula $C_7H_4O_3PCl$. The reaction can be expressed by the equation

$$C_6H_4\left\{\begin{array}{l}(1)\ COOH\\(2)\ OH\end{array}\right. + PCl_3 = C_7H_4O_3PCl + 2HCl.$$

We shall designate the new substance as *salicylo-phosphorous monochloride*, without thereby desiring to express an opinion concerning its constitution. The pure chloride melts at 36°–37°, boils at 127° under a pressure of about 11 mm., is easily soluble in ether, chloroform, and benzene, and smells, like many acid chlorides, of hydrochloric acid. It is decomposed violently by water into salicylic, phosphorous, and hydrochloric acids. An attempt to distill the substance under ordinary pressure showed that decomposition takes place at about 245°. It unites readily with chlorine and bromine, and reacts with phosphorus pentachloride, forming phosphorus trichloride and a substance of the composition $C_7H_4O_3PCl_3$.

Behavior of Salicylo-phosphorous Monochloride towards Phosphorus Pentachloride.

If the chloride be mixed with a molecular equivalent of phosphorus pentachloride, an energetic reaction takes place, the entire mass liquefies, and phosphorus trichloride, one of the resulting products, distills. The slightly yellow-colored liquid was rectified under diminished pressure. Two fractions were obtained, the first boiling at 78° and consisting of phosphorus trichloride, the second boiling at 168° (temperature of paraffin-bath 190°) under a pressure of about 11 mm. Analysis of this fraction showed that the substance has the same composition as that product obtained by the direct action of phosphorus pentachloride on salicylic acid, namely, *o*-$C_7H_4O_3PCl_3$. The formation may be represented by the equation

$$o\text{-}C_7H_4O_3PCl + PCl_5 = o\text{-}C_7H_4O_3PCl_3 + PCl_3.$$

It occurred to us from the behavior of the chloride $C_7H_4O_3PCl$ towards phosphorus pentachloride, that perhaps free chlorine or bromine would act in a similar manner.

Behavior of Salicylo-phosphorous Monochloride towards Chlorine and Bromine.

If dry chlorine be conducted over the chloride $C_7H_4O_3PCl$, it is absorbed with great energy and without evolution of gas. 19.0 grams chloride absorbed 6.7 grams chlorine (theory 6.6 grams). Towards the end of the operation the liquid assumed a yellowish color, due to an excess of chlorine. We can express the reaction as follows:

$$C_7H_4O_3PCl + Cl_2 = C_7H_4O_3PCl_3.$$

The product was rectified under diminished pressure. The main portion boiled constantly at 168° (temperature of paraffin-bath 190°) under a pressure of about 11 mm., and was found to be identical with those chlorides obtained by the action of phosphorus pentachloride on the chloride $C_7H_4O_3PCl$, or by the action of phosphorus pentachloride on salicylic acid.

The identity in the peculiarities of these chlorides will be seen from the following table:

	Boiling Point under about 11 mm.	Specific Gravity.
I. $C_7H_4O_3PCl_3$ from salicylic acid and PCl_5,	168° (temp. of bath 190°),	$d\frac{20}{4} = 1.55873.$
II. $C_7H_4O_3PCl_3$ from $C_7H_4O_3PCl$ and PCl_5,	168° (temp. of bath 190°),	$d\frac{20}{4} = 1.55868.$

Further, both chlorides exhibit similarity in their behavior towards water. As Moore and one of us[1] have already shown that the acid $C_7H_4O_3P(OH)_3$ could not be obtained in a pure condition from the chloride I with excess of water, we dissolved the chlorides I and II in dry benzene, and to each molecule of chloride added three molecules of water. In 24 hours the pure acid $C_7H_4O_3P(OH)_3$ had separated from the solutions. The acid from chloride I melted at 140°, while that from chloride II melted at 141°–142°. From these facts it follows that the two chlorides I and II are identical.

Not only chlorine but also bromine is absorbed with great avidity by the chloride $C_7H_4O_3PCl$. We added bromine till the resulting product had assumed a slight red color, an indication that the reaction was at an end. The formation of the new compound was accompanied by great evolution of heat; it was therefore found expedient to cool the substances during the operation. From the following data it will be seen that for every molecule of the chloride exactly one molecule of bromine was absorbed.

Experiment I. 14.2 grams chloride absorbed 10.8 grams bromine (theory 11.2).

Experiment II. 15 grams chloride absorbed 11.8 grams bromine (theory 11.9).

The reaction may evidently be expressed by the equation

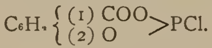
$$C_7H_4O_3PCl + Br_2 = C_7H_4O_3PClBr_2.$$

The new product, purified by rectification, boiled under a pressure of about 11 mm. at 185°–188°. It is a heavy, colorless, highly refractive liquid, and was found to have the specific gravity

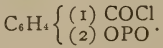
$$d\frac{20}{4} = 1.88522.$$

On the Constitution of Salicylo-phosphorous Monochloride and some of its Derivatives.

As regards the constitution of the compound $C_7H_4O_3PCl$, but two formulae can come under consideration if we keep in view its method of formation, change and decomposition:

I. 

$$C_6H_4\left\{\begin{matrix}(1)\ COO \\ (2)\ O\end{matrix}\right.\!\!>PCl.$$

II. 

$$C_6H_4\left\{\begin{matrix}(1)\ COCl \\ (2)\ OPO\end{matrix}\right..$$

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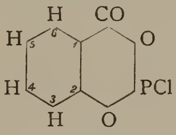
[1] Ann. Chem. (Liebig) **239**, 317.

According to formula I, the substance is an ortho-condensation-product. The bivalent rest PCl is joined to the carboxyl-oxygen atom as well as to the phenoxyl-oxygen atom, whereby a new ring consisting of six atoms is formed:



If the first constitutional formula be correct for the compound obtained by the action of phosphorus trichloride on salicylic acid, then by the action of phosphorus pentachloride or chlorine as well as bromine, two isomeric chlorides or bromides might be formed:

(*a*). $C_6H_4\left\{\begin{matrix}(1)\ COO\\(2)\ O\end{matrix}\right.\!>PCl_3.$ (*b*). $C_6H_4\left\{\begin{matrix}(1)\ COCl\\(2)\ OPOCl_2\end{matrix}\right..$

(*a'*). $C_6H_4\left\{\begin{matrix}(1)\ COO\\(2)\ O\end{matrix}\right.\!>PClBr_2.$ (*b'*). $C_6H_4\left\{\begin{matrix}(1)\ COCl\\(2)\ OPOBr_2\end{matrix}\right..$

If formula II be correct, then only the formulae (*b*) and (*b'*) would come under consideration.

As far as the methods of formation of these compounds $C_7H_4O_3PCl_3$ and $C_7H_4O_3PClBr_2$, as well as their behavior towards water are concerned, both formulae (*a*) and (*b*) are possible, and it is by no means improbable that, by the action of chlorine or bromine on the chloride $C_7H_4O_3PCl$, substances constituted like (*a*) and (*a'*) are first formed, which, on heating or distilling, or perhaps in the moment of formation, are changed into the compounds (*b*) and (*b'*).

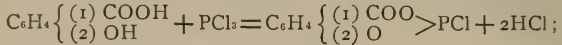
Notwithstanding our inability thus far to discover proofs that would establish the constitution of these substances beyond a doubt, we are inclined to look upon the chloride $C_7H_4O_3PCl$ as having the ring-formula

$$C_6H_4\left\{\begin{matrix}(1)\ COO\\(2)\ O\end{matrix}\right.\!>PCl,$$

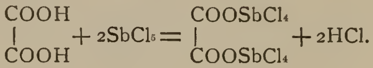
while, on the other hand, we believe the chloride $C_7H_4O_3PCl_3$ to have the constitution

$$C_6H_4\left\{\begin{matrix}(1)\ COCl\\(2)\ OPOCl_2\end{matrix}\right..$$

If the ring-formula be correct for the chloride $C_7H_4O_3PCl$, the action of phosphorus trichloride on salicylic acid is, to a certain extent, analogous to that of antimony pentachloride on oxalic acid:



$$C_6H_4\left\{\begin{matrix}(1)\ COOH\\(2)\ OH\end{matrix}\right. + PCl_3 = C_6H_4\left\{\begin{matrix}(1)\ COO\\(2)\ O\end{matrix}\right.>PCl + 2HCl;$$

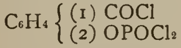
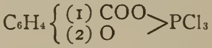


$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2SbCl_5 = \begin{matrix}COOSbCl_4\\|\\COOSbCl_4\end{matrix} + 2HCl.$$

However, as above stated, positive proofs that would establish the constitution of both chlorides are at present wanting. Neither by the action of methyl alcohol nor of phenol on the chloride *o*-$C_7H_4O_3PCl_3$ were we able to discover a smooth reaction.

But little better results were obtained by the action of zinc ethyl on the chloride $C_7H_4O_3PCl$. Upon treating the product of the reaction with potash solution, the unmistakable odor of the phosphines became very apparent. This fact seems to indicate that the chlorine in the chloride $C_7H_4O_3PCl$ is joined to the phosphorus atom.

The reason which leads us to prefer the formula

I.  $C_6H_4\left\{\begin{matrix}(1)\ COCl\\(2)\ OPOCl_2\end{matrix}\right.$ to the formula II.  $C_6H_4\left\{\begin{matrix}(1)\ COO\\(2)\ O\end{matrix}\right.>PCl_3$

lies in the comparison of the peculiarities of this chloride with those of the compound $(C_6H_5O)_2PCl_3$. In case the chloride *o*-$C_7H_4O_3PCl_3$ was constituted according to formula II, one might reasonably expect that it would easily decompose by distillation under diminished pressure, a behavior analogous to that of the chloride $(C_6H_5O)_2PCl_3$, which has already been described in the preceding paper. It does not, however, decompose; on the contrary, it may be distilled under greatly diminished pressure, and is at ordinary temperature liquid, while all the addition products of chlorine on

$C_6H_5OPCl_2$
$(C_6H_5O)_2PCl$, that is, the compounds
$(C_6H_5O)_3P$

$C_6H_5OPCl_4$
$(C_6H_5O)_2PCl_3$,
$(C_6H_5O)_3PCl_2$

are solids and are easily decomposed on heating under ordinary as well as diminished pressure. We are, therefore, of the opinion that the compound *o*-$C_7H_4O_3PCl_3$ is to be regarded as a derivative of phosphorus oxychloride rather than as a derivative of phosphorus pentachloride.

CHEMICAL LABORATORY, UNIVERSITY OF BONN, *June* 1, 1889.

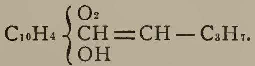
ON THE CONSTITUTION OF LAPACHIC ACID AND ITS DERIVATIVES.[1]

(Preliminary Communication.)

BY SAMUEL C. HOOKER AND WM. H. GREENE.

In 1857, Arnoudon[2] described, under the name taiguic acid, a yellow coloring matter existing in the Taigu wood of Paraguay; nine years later, Stein[3] described as greenhartin a similar matter which he had extracted from the greenheart of Surinam. In 1879, Paterno[4] proved the identity of these substances with the lapachic acid obtained by Siewert from the Lapacho tree of South America. Finally, we have recently found the same substance in a South African wood, the Bethabarra.[5]

Paterno,[6] in an admirable research published in 1882, has assigned to lapachic acid, with a very great degree of probability, the following constitutional formula:



$$C_{10}H_4 \begin{cases} O_2 \\ CH = CH - C_3H_7. \\ OH \end{cases}$$

Amylene-oxy-naphthaquinone.

The results from which this formula is mainly deduced are the following:

Lapachic acid gives a series of stable salts, but all experiments failed to reveal the true acid group, COOH.

On distillation with zinc dust, naphthalene and isobutylene were obtained.

On oxidation with nitric acid, phthalic acid was formed.

By reducing agents, a hydrolapachic acid was obtained, which rapidly absorbed oxygen, becoming reconverted into lapachic acid.

A monacetyl derivative was obtained.

Hydriodic acid and phosphorus gave a liquid hydrocarbon, which was taken to be amyl-naphthalene.

In the course of the study of this acid, Paterno prepared several compounds, which he was able to explain satisfactorily only by the assumption that two molecules of the acid had taken part in the formation of each of their molecules.

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[1] Read at the meeting of the Chemical Section of the Franklin Institute, held Tuesday, May 21, 1889.

[2] Comptes rendus **41**, 1152.

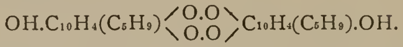
[3] J. prak. Chemie **99**.

[4] Gaz. Chim. Ital. **9**, 506.

[5] This Journal **11**, 267.

[6] Gaz. Chim. Ital. **12**, 337-392.

By the action of concentrated sulphuric acid on lapachic acid, a compound crystallising in beautiful red needles is formed, which has precisely the same percentage composition as lapachic acid. This compound, which is known as lapachone, was assigned the following formula by Paterno,



$$OH.C_{10}H_4(C_5H_9)\begin{matrix}\diagup O.O \diagdown \\ \diagdown O.O \diagup\end{matrix}C_{10}H_4(C_5H_9).OH.$$

Lapachone is insoluble in alkaline carbonates; it is soluble in caustic alkalies only after boiling for some time. According to Paterno, it separates from the alkaline solution on cooling, and is almost completely precipitated unchanged on the addition of acids.

While recently engaged on the study of the coloring matter of Bethabarra wood, subsequently proved by us to be lapachic acid, we obtained an orange-red quinone-like substance. In the course of our experiments with this compound we observed a number of reactions which, when we had afterwards identified the compound as lapachone, did not agree with Paterno's view of its constitution.

We found that lapachone shows many of the characteristics of a quinone. It gives a white crystalline compound with acid sodic sulphite, which is reconverted by acids and alkalies into the original substance. It forms compounds with hydroxylamine and ammonia with great readiness, and gives the quinone color reaction of Bamberger.

These reactions are obviously not reconcilable with the formula given above, and point to the probability that lapachone is $C_{15}H_{14}O_3$ and not $C_{30}H_{28}O_6$.

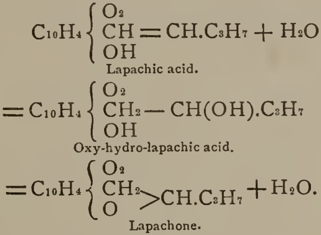
A determination of the molecular weight of lapachone, by Raoult's method, gave figures confirming this supposition, thus proving that only one molecule of lapachic acid is concerned in its formation, a result borne out by other facts.

Calculated for Paterno's formula $C_{30}H_{28}O_8$.	Calculated for $C_{15}H_{14}O_3$.	Found.
484	242	255

It remains, therefore, to explain how a substance having such strong acid tendencies as lapachic acid, dissolving with ease in alkaline carbonates, can be converted into an indifferent compound like lapachone, and yet retain the same percentage composition.

Although Paterno's formula of lapachic acid cannot be considered in any way proved, it lends itself well to the explanation of the formation of lapachone, and in this way considerable indirect proof is furnished of the probable correctness of Paterno's views in regard to lapachic acid.

It seems lawful to assume that under the influence of strong mineral acids (concentrated nitric acid in the cold acts similarly to concentrated sulphuric acid, as shown by Paterno), lapachic acid takes up a molecule of water, giving rise to an intermediate compound, which is at once decomposed by the acid, again splitting off water, but in a different direction. This is shown in the following equation:



$$C_{10}H_4\begin{cases}O_2\\ CH=CH.C_3H_7\\ OH\end{cases}+H_2O$$

Lapachic acid.

$$=C_{10}H_4\begin{cases}O_2\\ CH_2-CH(OH).C_3H_7\\ OH\end{cases}$$

Oxy-hydro-lapachic acid.

$$=C_{10}H_4\begin{cases}O_2\\ \left.\begin{matrix}CH_2\\ O\end{matrix}\right>CH.C_3H_7\end{cases}+H_2O.$$

Lapachone.

The fact that phthalic acid is produced by the oxidation of lapachic acid would appear to furnish proof that all the side groups are situated in the same benzene nucleus, and consequently whether lapachic acid be a derivative of α- or of β-naphthaquinone, the (OH) group must be in the ortho position to the amylene chain: this favors the probability of the occurrence of the above condensation.[1]

This view of the constitution of lapachone, *i. e.* regarding it as a derivative of naphthofurfuran, agrees very thoroughly with all its properties and reactions so far observed. It has, moreover, received direct confirmation from the result of an experiment, which was made to obtain, if possible, corroboration of our views.

Paterno states, as already mentioned, that lapachone is insoluble in caustic alkalies in the cold, but dissolves on heating, and is, in part, deposited from the filtered solution unchanged as it cools.

This observation seemed at variance with our idea of the constitution of lapachone, and we consequently carefully repeated Paterno's experiment. The insolubility of lapachone in alkaline carbonates and caustic alkalies in the cold is readily explained by the constitution we have assigned to it, and its solubility on boiling is best accounted for by the supposition that the furfuran ring is split by the action of potash, that one molecule of water is taken up with the formation of a salt of the compound

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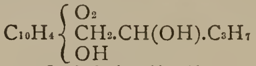
[1] It is, of course, possible, though scarcely probable, that lapachic acid is derived from β-β-naphthaquinone, in which case the relative positions of the amylene chain and the hydroxyl group would be the para.



$$C_{10}H_4\begin{cases}O_2\\CH_2.CH(OH).C_3H_7\\OH\end{cases}$$

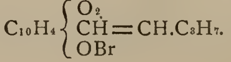
Oxy-hydro-lapachic acid.

which we had previously supposed to exist as an intermediate product in the formation of lapachone. This explanation proved quite satisfactory, for on neutralising with acetic acid, a red oil was obtained which, in the course of an hour or so, solidified to a yellow crystalline mass. Analysis proved it to have the expected composition. The tendency of the new substance to pass into lapachone under the influence of dilute mineral acids is very great, and hence if dilute hydrochloric acid be used for the precipitation, either a mixture of lapachone and the new compound, or lapachone only, is obtained.

We have not yet succeeded in preparing the potassium salt of the new substance in a crystalline form, but as its barium salt, which crystallises very readily in bright orange needles, closely resembles lapachone, it is not improbable that the potassium salt may have a similar appearance, which would account for Paterno's supposition that the crystals deposited on cooling and before the addition of hydrochloric acid were crystals of lapachone. It is right to add that the fusing point of these crystals was found by Paterno to be almost identical with that of lapachone.

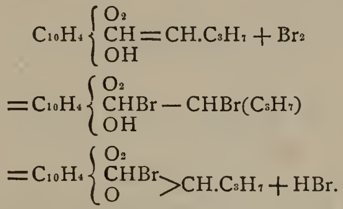
The salts of the new compound, as might be expected, dissolve to the same intense red color as those of lapachic acid. Oxyhydrolapachic acid melts at 125°, and is very readily soluble in most ordinary solvents. It may be obtained in comparatively large crystals by spontaneous evaporation of its solution in alcohol or acetic acid.

By the action of bromine on lapachic acid in acetic acid solution, Paterno obtained a compound which he regarded as monobromlapachic acid, and to which he assigned the formula



$$C_{10}H_4\begin{cases}O_2\\CH=CH.C_3H_7.\\OBr\end{cases}$$

Considering the properties of this compound and the probable constitution of lapachic acid, its formation would seem to be better explained by the supposition that an addition product is first formed, and that this, by splitting off hydrobromic acid, gives rise to the formation not of brom-lapachic acid but of brom-lapachone, thus:



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH=CH.C_3H_7+Br_2\\ OH\end{array}\right.$$

$$=C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr-CHBr(C_3H_7)\\ OH\end{array}\right.$$

$$=C_{10}H_4\left\{\begin{array}{l}O_2\\ \left.\begin{array}{l}CHBr\\ O\end{array}\right>CH.C_3H_7+HBr.\end{array}\right.$$

We are at present endeavoring to prove the truth of this supposition, and have already observed some important facts tending to show the correctness of our views.

The formation of several of the other compounds obtained by Paterno would appear to be better explained in a similar manner to the foregoing than by the formulae he has assigned to them. We prefer, however, to leave the discussion of these until our work has progressed further. In the meantime, we wish to say that, although we are hopeful further experiments will justify our present conclusions, we do not regard them as of necessity final, and have only been induced to make this preliminary communication to ensure to ourselves the undisturbed continuation of the work, which, owing to many causes, cannot, unfortunately, proceed with as great rapidity as we could desire.

POSTSCRIPT.—We have to-day (June 17) received from Prof. Paterno an advanced proof from No. 6 of the Gazzetta Chimica Italiana for this year, having reference to our intention, as stated in the AMERICAN CHEMICAL JOURNAL **II**, 267, of studying the constitution of lapachone. He requests that we desist from carrying out our purpose, as he is still investigating lapachic acid and its derivatives, a fact which should have been known to us, but unfortunately was not, owing to the miscarriage of a number of the Gazzetta for the current year, the only copy sent, to our knowledge, to Philadelphia. We gladly accede to Prof. Paterno's request, in full confidence that our work has not been without service in establishing the constitution of the derivatives of lapachic acid. At the time of writing, the above paper, which was read nearly a month ago, has been already printed for private distribution among the members of the chemical section of the Franklin Institute.

REDETERMINATION OF THE ATOMIC WEIGHT OF PALLADIUM.

By E. H. Keiser.

Among all the atomic weights there are few that have been so imperfectly determined as that of palladium. In 1826 Berzelius[1] found that 100 parts of the metal united with 28.15 parts of sulphur, from which proportion the value for the atomic weight of palladium would be 113.63. This number is undoubtedly too high, and two years afterwards the same investigator[2] obtained a much lower value as the result of two analyses of potassium palladious chloride, $PdCl_2.2KCl$. Weighed quantities of the salt were heated in a stream of hydrogen, and after reduction the quantities of metallic palladium and potassium chloride remaining were determined. The following are the results of the analyses:

I. 1.757 gram $PdCl_2.2KCl$ gave .575 gram Pd and .809 gram KCl.

II. 2.606 grams $PdCl_2.2KCl$ gave .851 gram Pd and .809 gram KCl.

	I.	II.
Pd,	32.726	32.655
KCl,	46.044	45.741
Cl (by difference),	21.230	21.604
	100.000	100.000

Calculating the atomic weight from the ratio of palladium to potassium chloride, the first analysis gives Pd = 105.7, the second Pd = 106.2.

In 1847 Quintus Icilius[3] determined the loss in weight which potassium palladious chloride undergoes when heated in a current of hydrogen, and found as the mean of three determinations that the amount of residue was 64.81 per cent., from which the calculated value for the atomic weight of palladium is 111.88. This value is undoubtedly too high.

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[1] Poggend. Annal. **8**, 177 (1826).

[2] Ibid. **13**, 454 (1828).

[3] F. W. Clarke, Recalculation of the Atomic Weights, p. 257.

No other determinations of this atomic weight have been made. The values that have been adopted by those who have recalculated the atomic weights are as follows:

Meyer and Seubert, . .	$(O=15.96)$	106.2
F. W. Clarke, . . .	$(O=15.96)$	105.7
W. Ostwald, . . .	$(O=16)$	105.9
Van der Plaats, . .	$(O=16)$	106.5

As these values are calculated from the two analyses of Berzelius mentioned above, and as these analyses do not agree very closely with one another, it seemed to me to be desirable to undertake a new series of determinations of this atomic weight. It also appeared advisable to analyse a different compound from that employed by Berzelius, for the reason that, as stated in his paper, it is extremely difficult to get the potassium palladious chloride free from water. The crystallised salt when dried in a desiccator for a long time still retains water of decrepitation (verkinsterungswasser), nor can it be completely removed by drying in an air-bath at a low temperature; while if the temperature be raised, partial decomposition takes place and hydrochloric acid and palladium oxide are formed.

For the purpose of avoiding this source of error, experiments were at first made with the double chlorides of palladium and ammonium. Ammonium palladious chloride, $PdCl_2 2NH_4Cl$, and ammonium palladic chloride, $PdCl_4.2NH_4Cl$, were prepared and purified by repeated recrystallisation, and were then dried in a partial vacuum over sulphuric acid. Portions of the salts were weighed off in platinum boats and heated in an air-bath. It was found that the salts gradually lost in weight as the temperature increased, and it was impossible to obtain a constant weight at temperatures below the point of decomposition. The dried salts also proved to be very hygroscopic, they absorbed moisture so rapidly on the scale pan that it was impossible to weigh them with the accuracy that is necessary in atomic weight determinations. All hope of using these compounds was abandoned, and the same objections were found to apply to the double chlorides of palladium and sodium. Indeed, it appears that the double chlorides of the alkali and platinum metals all contain water of decrepitation which it is extremely difficult if not impossible to remove, and which makes them unsuited for atomic weight determinations. Stas[1] gave up his attempt to determine the atomic weight of platinum by reduction of potassium platinic chloride when he found that the carefully dried salt still retained a trace of moisture. Berzelius had previously observed the same fact, and he found that the double chlorides of the alkali and other platinum metals also contain water. In some of his analyses he endeavored to remove this trace of water by heating the salts in a stream of chlorine, and this method of drying was afterwards employed by Seubert[2] in his determination of the atomic weight of iridium.

After examining the properties of a number of palladium compounds, I found that the yellow crystalline palladium diammonium chloride, which is formed whenever hydrochloric acid is added to a solution of palladium chloride in an excess of ammonia, is a much more suitable compound for the purpose of atomic weight determinations than any of those mentioned above. It possesses the advantages of being a stable compound which can be prepared in a state of great purity. It contains no water of crystallisation, nor does it retain water mechanically which cannot be removed by drying the compound in a desiccator. The salt can be dried in an air-bath without undergoing decomposition, and further, the dried compound is not hygroscopic and can be accurately weighed in the atmosphere of the balance-case. Heated in a stream of hydrogen, it at first absorbs the gas, the bright yellow color changes to black, and metallic palladium and ammonium chloride are formed. On raising the temperature, the ammonium chloride is volatilised and spongy palladium remains behind.

Preparation of Palladium Diammonium Chloride.

Metallic palladium in the form of foil was dissolved in aqua regia and the solution evaporated to dryness. The residue of palladious chloride was dissolved in dilute hydrochloric acid, and the solution, after filtering, was treated with ammonia and heated until the flesh-colored precipitate which was at first formed had been dissolved by the excess of ammonia. The liquid was then again filtered to remove a trace of ferric hydroxide, and into the filtrate hydrochloric acid gas was passed until the palladium diammonium chloride was completely precipitated. The yellow precipitate was thereupon redissolved in ammonia to separate it from any of the analogous rhodium compound which might have been present, and to the filtrate hydrochloric acid was added to reprecipitate the palladium diammonium chloride. The precipitate was dried and afterwards heated in a current of pure hydrogen. Pure spongy palladium was thus obtained, which was converted into the yellow crystalline palladium diammonium chloride by the process just described. The compound was dried at first over sulphuric acid, afterwards in the air-bath at a temperature of from 120° to 130°.

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[1] Stas, Chemische Proportionen, 1867, p. 265.

[2] Ber. d. chem. Ges. **11**, 1770.

Analyses of the palladium diammonium chloride were made by weighing off portions of the dried salt in platinum boats and introducing the boats into a short combustion tube which was connected with an apparatus for the preparation of pure hydrogen. The gas was prepared by the interaction of pure zinc and dilute sulphuric acid. It was purified by passing through acid and alkaline potassium permanganate, then through concentrated sulphuric acid, over iron wire heated to a red heat, and finally over phosphorus pentoxide. After the air had been expelled from the combustion tube by the stream of hydrogen, that part of the tube which contained the platinum boat was heated gently. At a comparatively low temperature the yellow palladium diammonium chloride begins to turn black, the change is accompanied by a rapid absorption of hydrogen, and metallic palladium and ammonium chloride are formed,

$$PdN_2H_6Cl_2 + 2H = Pd + 2NH_4Cl.$$

So readily does this change take place that it is only necessary to heat one end of the boat until the action begins, because the heat of the reaction is sufficient to convert the entire quantity of the compound into metallic palladium and ammonium chloride.

After the reduction the temperature of the combustion tube was gradually raised until the ammonium chloride was all volatilised and nothing but spongy palladium remained in the boat. The finely divided palladium usually adheres together and forms a porous bar having the shape of the interior of the boat. The boat was now allowed to cool down, at first in the stream of hydrogen until it was below a red heat, then after a time the hydrogen was displaced by a current of dry air. By this means it was possible to avoid the retention of the hydrogen by the palladium, and as the hydrogen was not displaced by the air until the temperature had fallen considerably below a red heat, it was not possible that palladium oxide should have been formed. After the boat had acquired the temperature of the air, it was removed from the combustion tube and the weight of metallic palladium remaining in it determined.

A short beam analytical balance, sensitive to $\frac{1}{20}$ milligram, and an adjusted set of weights were employed for all the weighings. The correction of the weights for buoyancy of the air was found to be smaller than the experimental errors, and was therefore omitted. From the results of the analyses the atomic weight of palladium was calculated by means of the proportion:

$$A : B :: x + 104.76 : x \quad \text{or}$$

$$x = \frac{104.76\ B}{A - B}\text{, in which}$$

$A =$ weight of $PdN_2H_6Cl_2$ taken,
$B =$ " Pd found, and

$104.76 = N_2 + H_6 + Cl_2 = (14.01 \times 2) + (1 \times 6) + (35.37 \times 2)$.

The results of the analyses are as follows:

I Series.

Number.	Weight of $PdN_2H_6Cl_2$ taken.	Weight of Pd obtained.	Atomic Weight.
1	.83260	.41965	106.459
2	1.72635	.86992	106.410
3	1.40280	.70670	106.355
4	1.57940	.79562	106.342
5	1.89895	.95650	106.321
6	1.48065	.74570	106.292
7	1.56015	.78585	106.322
8	1.82658	.92003	106.317
9	2.40125	1.20970	106.355
10	1.10400	.55629	106.400
11	.93310	.47010	106.366
Total, .	16.74583	8.43606	[106.3520]

Mean value, 106.352

Maximum 106.459
Minimum 106.292

Difference, .167

II SERIES.

The palladium diammonium chloride used in this set of determinations was prepared from the metallic palladium which was obtained in the first series of determinations.

Number.	Weight of $PdN_2H_6Cl_2$ taken.	Weight of Pd obtained.	Atomic Weight.
1	2.61841	1.31900	106.340
2	2.23420	1.12561	106.366
3	1.73553	.87445	106.325
4	1.69160	.85210	106.390
5	1.72403	.86825	106.332
6	1.12222	.56535	106.286
7	1.17457	.59200	106.355
8	2.42760	1.22280	106.455
Total, .	14.72816	7.41956	[106.3503]

Mean value, 106.35

Maximum 106.455
Minimum 106.286

Difference, .169

The mean value of both series of determinations is 106.35, a number which agrees fairly well with that calculated from the second analysis of Berzelius, mentioned at the beginning of this article.

BRYN MAWR, PA., *June*, 1889.

ON THE ACTION OF DILUTE ACIDS ON BENZOIC SULPHINIDE AND THE ANALYSIS OF COMMERCIAL SACCHARIN.

BY IRA REMSEN AND W. M. BURTON.

In the course of experiments undertaken by us for the purpose of studying the effect of nascent hydrogen on benzoic sulphinide,[1] we noticed that when this compound is boiled with dilute hydrochloric acid and tin its sweet taste is soon destroyed. Further study showed that the change is due to the action of the acid alone, and that no reduction takes place. Two grams of the pure sulphinide were boiled with about 100 cc. hydrochloric acid diluted with fifteen times its volume of water. After forty-five minutes the sweet taste of the solution had disappeared. Pure silver oxide was then added in excess to remove the hydrochloric acid, and, after filtering, hydrogen sulphide was passed through the filtrate, when a considerable precipitate of silver sulphide was formed. On evaporating the filtrate from this, a small quantity of white crystals was deposited. These proved to be ortho-sulphamine-benzoic acid. The mother liquor was further concentrated until fine large crystals of acid ammonium ortho-sulphobenzoate were deposited. These were easily recognised by their crystalline form, melting point, and the fact that they gave off ammonia when treated with caustic alkalies. From the 2 grams of sulphinide taken we obtained about .1 gram *o*-sulphamine-benzoic acid and 1½ grams of the acid ammonium salt. It appears, therefore, that when benzoic sulphinide is boiled with hydrochloric acid it is converted into *o*-sulphamine-benzoic acid and acid ammonium *o*-sulphobenzoate. Further experiments showed that by continued boiling with hydrochloric acid all the *o*-sulphamine acid is converted into the acid ammonium salt. Probably the first result of the action of the hydrochloric acid is represented by this equation:

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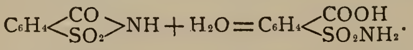
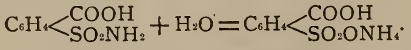
[1] It was hoped that a basic substance might be formed, as when phthalimide is reduced. No evidence of reduction was obtained by boiling with tin and hydrochloric acid. On the other hand, sodium amalgam causes deep-seated changes, as was shown by the abundant evolution of sulphur dioxide and hydrogen sulphide when the solution is acidified. No definite product, however, was isolated.



$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH + H_2O = C_6H_4<\begin{matrix}COOH\\SO_2NH_2\end{matrix}.$$

Then by continued boiling the second change takes place as represented in this equation:



$$C_6H_4<\begin{matrix}COOH\\SO_2NH_2\end{matrix} + H_2O = C_6H_4<\begin{matrix}COOH\\SO_2ONH_4\end{matrix}.$$

A series of experiments was now undertaken to determine what strength of acid and what conditions are best for the rapid and complete conversion of the sulphinide into the acid ammonium salt. Hydrochloric acid of various degrees of concentration was prepared by diluting the pure strong acid (sp. gr. 1.17) with different amounts of water. In each experiment 100 cc. of a dilute acid of known strength were placed in a balloon flask of 250 cc. capacity, and the flask connected with an upright condenser. The mixture was gently boiled, and from time to time it was tested by the taste to ascertain just when the sweet taste disappeared. The test is as refined as any that could be devised, as the presence of a weighable quantity of the sulphinide in the solution can be detected in this way without difficulty. Of course, the disappearance of the sweet taste is not proof that the sulphinide has been converted into the acid ammonium salt, for, as we have seen, some *o*-sulphaminebenzoic acid is always formed. Still the quantity of this formed is quite insignificant.

The following table gives the results of the experiments:

Concentration of Acid. HCl : H_2O	Time.
1 : 100	6 hours,
1 : 75	3 " 15 min.
1 : 50	2 " 15 "
1 : 25	2 "
1 : 20	1 "
1 : 15	45 min.
1 : 10	30 "
1 : 5	40 "
1 : 8	30 "

According to this, the hydration of benzoic sulphinide is best effected by hydrochloric acid prepared by diluting the pure strong acid of specific gravity 1.17 with 8–10 parts water. Special experiments showed that the change is effected slowly by the concentrated acid on a water-bath, though by heating in a closed vessel to 150° the change takes place rapidly.

Analysis of Commercial Saccharin.

The easy conversion of benzoic sulphinide into a substance which is readily soluble in water suggested a method for determining the amount of the sulphinide contained in commercial saccharin. As is well known, this product is manufactured by oxidising toluene sulphonamide. According to the statements made in regard to the process, the orthotoluene sulphonchloride is separated from the para-compound and is then converted into the amide, which is oxidised with potassium permanganate. It is, however, a difficult and expensive matter to effect a complete separation of the two chlorides. If the separation is not complete, then both sulphonamides will of course be formed, and the separation of these is even more difficult than that of the chlorides. When the mixture of the two amides is oxidised with potassium permanganate, the ortho-amide is converted mainly into the sulphinide, and, to some extent, varying with the conditions, into acid potassium ortho-sulphobenzoate, while the para-amide is converted into para-sulphamine-benzoic acid. A consideration of these facts makes it appear probable that commercial saccharin contains at least the three substances, benzoic sulphinide, para-sulphamine benzoic acid, and acid potassium ortho-sulphobenzoate, with perhaps some of the sulphonamides remaining unoxidised. Attempts made in this laboratory to prepare pure benzoic sulphinide from commercial saccharin have repeatedly shown that the amount of para-sulphamine acid present in it is very considerable, amounting as nearly as could be judged to about 50 per cent. of the whole. But no careful experiments were undertaken to determine the amount, owing to the lack of a suitable method of analysis. Briefly stated, the method which we used consists in boiling the commercial saccharin with an excess of hydrochloric acid prepared by diluting the pure strong acid with eight times its volume of water. By this means the sulphinide is converted quantitatively into the acid ammonium salt of *o*-sulphobenzoic acid, while the *p*-sulphamine-benzoic acid and the acid potassium salt of *o*-sulphobenzoic acid which are always present in commercial saccharin remain unchanged. The para-acid is very difficultly soluble in cold water, while the potassium and ammonium salts of *o*-sulphobenzoic acid are very easily soluble in cold water. If, therefore, the liquid obtained by boiling commercial saccharin with hydrochloric acid is evaporated to a small volume and allowed to cool, practically all the para-sulphamine-benzoic acid will be on the filter while the potassium and ammonium salts of *o*-sulphobenzoic acid will be in the filtrate. This can then be evaporated to dryness and the weight of the salts determined. By determining the potassium in the residue, and calculating the weight of acid potassium salt, the weight of the acid ammonium salt can be estimated, and from this the weight of the benzoic sulphinide corresponding to it. It may be questioned whether it is fair to assume that all the potassium found is present in the form of the acid potassium salt of *o*-sulphobenzoic acid. With reference to this point we can only say that we excluded the salts of mineral acids; that in working over large quantities, amounting to several kilograms of the commercial saccharin, we have isolated the acid potassium salt in well-formed crystals, and that we have never found any other potassium salt. That there was no ortho-compound left on the filter was shown by special experiments. The para-acid was compared with pure acid obtained by oxidising *p*-toluene sulphonamide. The two were found to conduct themselves alike as regards fusion, solubility, and crystallisation. It was fused with potassium hydroxide and converted into para-oxybenzoic acid, melting sharply and crystallising well in the characteristic form. Not a trace of salicylic acid was formed, ferric chloride producing no marked change in color.

The para-acid is not changed by boiling with dilute hydrochloric acid.

The most convenient method for the analysis of commercial saccharin was found to be as follows:

About 2 grams saccharin is placed in a balloon flask of 250 cc. capacity, 100 cc. hydrochloric acid (1–8) added, and the flask connected with an inverted condenser. The mixture is then gently boiled for an hour. The clear solution in the flask is then transferred to an evaporating dish and evaporated to about 15 cc. This is allowed to stand for several hours, when the parasulphamine acid separates in glistening scales. This is collected on a filter previously dried to a constant weight at 80°. The acid is thoroughly washed with cold water, and then dried to constant weight at 80°. The filtrate and washings are collected in a weighed glass evaporating dish, evaporated to dryness and weighed. The amount of potassium in this residue is determined by treating a weighed portion of it in a platinum crucible with strong sulphuric acid, and weighing as potassium sulphate. Five parallel analyses of two samples of saccharin were made, and the results are given in the tables below. Sample I was imported in 1887 and sample II in 1888.

Analysis of Sample I.

No.	Amt. Taken.	*p*-Acid.	Ac.K Salt.	Ac.NH_4 Salt	= Sulphinide.
1.	1.3605	0.6693	0.0979	0.6906	0.5771
2.	1.9304	0.9721	0.1340	0.9867	0.8245
3.	2.3258	1.1326	0.1677	1.2021	1.0044
4.	1.7608	0.8980	0.1254	0.9229	0.7711
5.	2.1354	1.0837	0.1520	1.0780	0.9007

Analysis of Sample II.

No.	Amt. Taken.	*p*-Acid.	Ac.K Salt.	Ac.NH_4 Salt	= Sulphinide.
1.	2.2684	0.9933	0.1837	1.3209	1.1037
2.	2.2860	1.0058	0.1778	1.2864	1.0765
3.	2.1358	0.9666	0.1687	1.2256	1.0241
4.	1.8756	0.8155	0.1499	1.0823	0.9044
5.	2.0955	0.9383	0.1674	1.2170	1.0169

The above results when expressed in percentages give the following figures:

Composition of Sample I.

	I.	II.	III.	IV.	V.
Parasulphamine-benzoic acid,	49.20	50.36	48.70	51.01	50.75
Benzoic sulphinide,	42.42	42.71	43.19	43.80	42.18
Ac. potass. *o*-sulphobenzoate,	7.20	6.94	7.21	7.12	7.12

Composition of Sample II.

	I.	II.	III.	IV.	V.
Parasulphamine-benzoic acid,	43.79	45.13	45.26	43.48	44.78
Benzoic sulphinide,	48.65	48.29	47.95	48.22	48.53
Ac. potass. *o*-sulphobenzoate,	8.10	7.98	7.90	7.99	7.99

In analyses of IV and V of each sample the potassium was not determined, but the mean of the results obtained in analyses I, II and III was taken. While owing to the nature of the substances and the imperfection of the method the results are not as concordant as could be desired, they are nevertheless close enough to give confidence in the method, and it may be asserted with perfect confidence that the figures are very near the truth.

It follows that the substance known commercially as *saccharin is a mixture of para-sulphamine-benzoic acid, benzoic sulphinide, and acid potassium o-sulphobenzoate, and that the amount of the sulphinide present is somewhat less than* 50 *per cent.*

As is well known, the only one of the three constituents of saccharin which is regarded as having any commercial value is the sulphinide, and its value is due to the fact that it has about three hundred times the sweetening power of cane sugar. We think that this estimate is somewhat too high, but assuming it to be correct, and assuming further that only about 50 per cent. of the commercial substance is sulphinide, an assumption that is fully justified by our analyses, it follows that commercial saccharin instead of being "three hundred times as sweet as sugar" is not more, and is probably considerably less, than one hundred and fifty times "as sweet as sugar." It would, we think, be nearer the truth to say that commercial saccharin has a sweetening power about one hundred and twenty-five times as great as that of cane sugar.

ON THE DETERMINATION OF CHLORINE IN WATER.

By Allen Hazen.

Chlorine is almost always determined in water by titration with silver nitrate solution, using potassium chromate as indicator. It has been my practice to titrate fifty cubic centimeters of water or sewage in a porcelain dish with a silver solution of such strength that one cubic centimeter corresponds to half a milligram of chlorine, so that each cubic centimeter used represents one part of chlorine in 100,000. The results commonly obtained by this method are somewhat too high, owing to the fact that the red color of silver chromate does not become perceptible until a certain excess of silver has been added, and this excess, as will be shown, is much too large to be neglected when close work is desired.

I have made a large number of experiments to ascertain the amount of excess of silver solution required to give an end-point under various conditions of titration, and especially to find the influence of the volume of the liquid titrated, the amount of chromate used, and the amount of precipitated silver chloride present. I have found that under constant conditions the required excess is constant, and that by making the proper corrections very accurate results can be obtained, even in widely differing conditions of titration.

The general method by which these experiments have been carried out is as follows: Silver and chlorine solutions were made by dissolving the theoretical quantities of pure silver nitrate and sodium chloride in distilled water. A solution of potassium chromate, free from chlorine, was used which contained 0.12 gram per cubic centimeter. Measured quantities of chlorine and chromate solutions were put into a white porcelain dish with distilled water, and titrated with the silver solution. The amount of silver solution required was in every case more than an équivalent of the salt used. The excess is the amount of silver solution required to produce an end-point under the conditions of the experiment. In all cases I have not gone beyond an end-point which was as faint as could be seen with certainty after some seconds, there being always a second dish of chromate, for comparison, by the side of that in which the titration is made. The solution should not be so concentrated as to make the precipitated silver chloride coagulate, as in that case the required excess is somewhat greater than otherwise.

The amount of chromate used has a considerable influence on the result, especially in a large volume. In general, it may be said that the greater the amount of chromate used, the smaller will be the required excess of silver; but when the quantity has reached a certain point, the advantage gained by any further increase is more than overcome by the increase in color, which obscures the exact end-point. I have found 0.0010 gram potassium chromate per cubic centimeter of liquid titrated (a much larger amount than is generally recommended) to be a suitable quantity. This is enough to give most of the advantage due to increased quantity, while the end-point remains very sharp. In practice I use 0.06 gram of potassium chromate in all cases, even when the volume of liquid titrated is small; the end-point is quite as sharp as with a smaller quantity.

The following titrations show the excess of silver solution required when different quantities of chromate are used, all other conditions being the same:

NaCl sol. taken.	K_2CrO_4 grams.	Vol. of liquid titrated.	$AgNO_3$ sol. required.	Excess.
2 cc.	.004	50 cc.	2.45	.45
"	.008	"	2.35	.35
"	.016	"	2.27	.27
"	.030	"	2.20	.20
"	.060	"	2.16	.16
"	.120	"	2.15	.15

The volume of the liquid titrated has also an influence on the result. (The volume may be easily determined, after titration, by pouring the liquid into a graduate.) The required excess of silver solution increases regularly with the volume, and when 0.06 gram chromate is used, and the volume is not more than 60 cc., this excess may be represented by the formula $x = .003\ v + .02$, where v is the volume of liquid at the end of the titration in cubic centimeters. Thus with a volume of 3 cc. the correction is .03 cc., while with a volume of 50 cc. the correction is .17 cc.

The following titrations were made in different volumes, all other conditions being the same:

NaCl sol. taken.	K_2CrO_4 used.	Vol. of liquid.	$AgNO_3$ sol. required.	Excess.
2 cc.	.06 gr.	4 cc.	2.03 cc.	.03 cc.
"	"	10	2.05	.05
"	"	20	2.07	.07
"	"	30	2.10	.10
"	"	40	2.14	.14
"	"	50	2.17	.17
"	"	100	2.35	.35

The amount of precipitated silver chloride present influences the result. The required excess of silver solution, in addition to the correction for volume, increases regularly with the amount of precipitated silver chloride, and is nearly proportional to the amount of silver solution used. The correction is nearly one per cent. of the volume of the silver solution. The most convenient way to apply this correction is to use a silver solution containing one per cent. more than the theoretical amount of silver. If the silver solution is standardised against sodium chloride, it will be of this strength, and no correction will be required for the amount of precipitate. If the amount of chlorine titrated is very low the results are somewhat irregular, so that if less than 1 cc. of silver solution is required for 50 cc. of water, I prefer to run in 1 cc. of salt solution and deduct the equivalent of silver solution from the result. The influence of the amount of precipitated silver chloride is shown by the following titrations:

NaCl sol. taken.	K_2CrO_4 used.	Vol. of liquid.	$AgNO_3$ sol. required.	Excess.
0.0 cc.	.06 gr.	50 cc.	.10 cc.	.10 cc.
.2	"	"	.30	.10
.6	"	"	.72	.12
1.0	"	"	1.16	.16
2.99	"	"	3.17	.18
5.98	"	"	6.19	.21
9.97	"	"	10.22	.25

The silver solution used for these titrations was very carefully made to contain exactly the theoretical quantity of silver. A portion of this solution was precipitated with its equivalent of salt solution; to the clear liquid, separated from the precipitate, was added a small amount of salt solution and chromate, and titrated with silver solution. The amount required was the same as when distilled water was used, all other conditions being the same.

Although the original silver solution was made by dissolving the theoretical quantity of pure silver nitrate in water, it is practically more convenient and better to depend upon titrations of salt solution for its strength, always making the correction for volume. As has been shown, a solution made in this way will require no correction for precipitated silver chloride, but the correction for volume must invariably be applied. As this correction is not at all proportional to the amount of silver solution used, accurate results cannot be obtained by using a stronger solution and omitting this correction.

A few titrations of salt solution in varying amounts of water, taken at random from my note-book, are as follows. The silver solution used was standardised against salt solution, and the correction for volume made. In each case .06 gram chromate was used.

Milligrams Cl taken.	Vol. of liquid.	$AgNO_3$ sol. required.	Corrected for volume.	Milligrams Cl found.
5	16 cc.	10.06	9.99	4.995
5	50	10.18	10.01	5.005
1	40	2.12	1.98	.99
1	70	2.20	1.99	.995
.94	80	2.10	1.84	.92
1.53	46	3.26	3.10	1.55
1.30	30	2.75	2.64	1.32
.87	4	1.76	1.73	.865
2.24	45	4.62	4.47	2.235
9.20	65	18.70	18.48	9.24
3.76	22	7.68	7.59	3.795
.46	60	1.10	.90	.45
3.15	35	6.46	6.34	3.17
1.65	50	3.45	3.27	1.635

It is possible, by direct titration in this way, to get results within .05 part chlorine per 100,000 in clear waters, when the chlorine is not higher than 10 parts. When the chlorine is low and greater accuracy is required, the water must be concentrated before titration. When this is done, there must invariably be added an excess of sodium carbonate before evaporation, as otherwise there may be a serious loss of hydrochloric acid, even if the residue is not allowed to go to dryness. Commonly 0.02 gram of sodium carbonate, or less, is sufficient, and this quantity does not in the least interfere with the titration. If too much has been used, calcium nitrate may be added before titration. An excess of nitrate does not influence the result.

I have concentrated waters in three ways, any one of which gives perfectly reliable results. First, by boiling down 500 cc. or more in a flask with sodium carbonate, to about 50 cc. By this method there is no possibility of hydrochloric acid being absorbed from the air. It is very convenient, and gives good results when there is not too much organic matter present. In such cases the residue becomes too brown for sharp titration, and must be decolorised by aluminium hydrate and filtered.

Second, by evaporation on a water-bath with sodium carbonate, to a small bulk.

Third, by treating the solid residue of evaporation. All determinations of solids in this laboratory are made with the addition of sodium carbonate, and the ignition is made in a radiator.[1] I have found by a large number of determinations that there is no loss of chlorine whatever by igniting in this way, while all organic matter is destroyed. After the residue is weighed, the chlorides may be extracted with hot water, and transferred to a porcelain dish and titrated. When much organic matter is present, this seems to be the most accurate method, and in all cases it is very convenient. Care must be taken that no hydrochloric acid is absorbed during evaporation, and that all chlorine is washed from the residue.

The following determinations are given as illustrations of the different methods, and the correction for volume:

Serial No.	Amt. taken.	Vol. of liquid.	NaCl sol. used	$AgNO_3$ sol. required.	$AgNO_3$ corrected for vol.	Parts per 100,000.	Remarks.
		55	10	10.20	10.02		Standardisation.
2691	50	53	1 cc.	1.30	.12	.12	Direct titration.
"	500	45	0	1.53	1.38	.138	Boiled down in a flask.
"	250	20	0	.80	.72	.144	Evaporated on a water-bath.
"	250	15	0	.74	.68	.136	Solid residue.
2689	50	53	1	1.35	.17	.17	Direct titration.
"	500	50	0	1.65	1.48	.148	Boiled down in a flask.
"	250	20	0	.80	.72	.144	Evaporated on a bath.
"	200	15	0	.65	.59	.147	Solid residue.
2794	50	53	1	1.50	.32	.32	Direct titration.
"	100	15	0	.75	.68	.34	Solid residue.
2809	50	56	0	5.40	5.21	5.21	Direct titration.
"	100	30	0	10.55	10.44	5.22	Solid residue.
2821	50	58	0	7.53	7.34	7.34	Direct titration.
"	50	20	0	7.38	7.30	7.30	Solid residue.

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[1] See T. M. Drown, Tech. Quarterly, Dec. '88; Chem. News **59**, 82.

No. 2691 is a sample of the city water of Lawrence; No. 2689 is a sample of city water filtered through sand; Nos. 2794 and 2809 are other clear waters, and No. 2821 is a sample of sewage.

I have made duplicate determinations of chlorine by two or more of these methods in several hundred samples of water and sewage, with exceedingly regular results, and there appears to be no source of constant error.

LAWRENCE EXPERIMENT STATION, MASS. STATE BOARD OF HEALTH.

ON ACETO-METANITROBENZOIC ANHYDRIDE.[1]

BY WILLIAM H. GREENE.

In the reaction of acetyl chloride with silver metanitrobenzoate, L. Liebermann[2] claimed to have obtained metanitrobenzoyl acetic acid, a reaction which would be inexplicable and without analogy. In the course of another investigation Bischoff and Rach[3] took the opportunity of studying the action of acetyl chloride on the silver salt of *o*-nitrobenzoic acid, and found that the reaction did not take place in the sense indicated by L. Liebermann.

Under the name acetylmetanitrobenzoic anhydride, Beilstein in his *Organische Chemie* (**2**, 786) describes the product supposed by Liebermann to be metanitrobenzoyl acetic acid, but the properties mentioned accord as little with those which this anhydride should exhibit, as with those which would be expected in the acid Liebermann thought he had obtained.

A preparation of this compound, according to the directions of Liebermann, by the addition of dry silver metanitrobenzoate to an excess of cold acetyl chloride, and pouring the product into water, yielded an acid fusing between 126° and 137°. 0.1866 gram of the silver salt of this acid yielded 0.0731 gram silver.

Ag found, 39.17 per cent. Ag calculated for nitrobenzoate, 39.42 per cent.

The acid is metanitrobenzoic, regenerated from the silver salt employed.

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[1] Read at the stated meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

[2] Ber. d. chem. Gesell. **10**, 863.

[3] Ibid. **17**, 2799.

By the reaction of sodium metanitrobenzoate with acetyl chloride, extraction of the product with absolute ether, and evaporation of the latter, aceto-metanitrobenzoic anhydride can be readily obtained, as also by exposing silver metanitrobenzoate to the vapor of acetyl chloride and extracting with absolute ether in the same manner. It crystallises in colorless needles, fusible at 45°, and remaining fused at a much lower temperature. It is insoluble in water, by which it is not at once decomposed when crystallised, so that it may be washed with dilute sodium carbonate and water and quickly dried between filter papers without change. The presence of either alcohol or water in the ether used for extraction results in the complete decomposition of all the anhydride.

REVIEWS AND REPORTS.

AUS JUSTUS LIEBIG'S UND FRIEDRICH WÖHLER'S BRIEFWECHSEL IN DEN JAHREN 1829–1873. Unter Mitwirkung von Fräulein EMILIE WÖHLER herausgegeben von A. W. HOFMANN. Zwei Bände. Braunschweig, 1888. Vieweg.

Rarely have chemists been given such a treat as is afforded by these remarkable letters of Liebig and Wöhler. As indicated in the title, they cover a period of forty-four years, beginning in 1829, when Liebig was 26 years old and Wöhler 29, and ending in 1873, when Liebig died. It appears that the correspondence was begun in consequence of the fact that both chemists were working on certain derivatives of cyanogen. The first letter has reference to the relations between cyanuric acid and cyanic acid. Soon afterwards Wöhler suggests that they should undertake a piece of work together, he to work in Berlin and Liebig in Giessen. "Ich überlasse die Wahl des Gegenstandes ganz Ihnen," he writes. Liebig is heartily pleased by the suggestion, and proposes an investigation on the action of sulphur chloride on ammonia. Wöhler is obliged to decline this, as he dare not work with chlorine; but he suggests the desirability of working up mellithic acid, and a week later Liebig communicates the first results of his investigation. Soon afterwards they began a piece of work on cyanic acid which occupied them for some time.

In 1832 we find them working on the oil of bitter almonds, a subject suggested by Wöhler. On May 30 he writes: "Dass dir die Aufgabe Bittermandelöl gefällt, freut mich. Nun rasch daran." On July 12 again: "Ich habe vorläufig schon allerlei Versuche damit vorgenommen, ohne zu einem präcisen Resultate gekommen zu sein. Es scheint ein harter Nuss zu sein." But on August 30, after the two friends had worked together for a few weeks, Wöhler again writes: "Ich sende Dir anbei die Bittermandelöl-Abhandlung." This great research, which exerted a controlling influence on the thoughts of chemists and formed the foundation of the radical theory, was first suggested on May 30, and the work was completed and the memoir written by August 30 of the same year. In the following year (1833) the effect of this paper was already apparent to the authors. Liebig writes, March 15, 1833: "Die Pariser sind über diese Abhandlung ganz toll. Pelouze schreibt mir: 'On ne parle plus à Paris dans le monde chimique que de vos experiences. Venez donc avec M. Wöhler, venez-y recevoir le tribut d'hommages qui vous est dû.'"

Liebig's quick temper and his harsh criticisms were a constant source of anxiety to Wöhler, who made frequent though ineffectual efforts to calm his friend. A few extracts will indicate his method: "Du hast mich misverstanden. Ich habe ja nicht gemeint, dass Du Deine Ansichten, wenn sie von denen Anderer abweichen, zurückhalten sollst, das wäre ja verrückt von mir, sondern ich habe nur gewünscht, dass Du Deinen Widerspruch in eine etwas andere, minder verletzende Form einkleiden mögest. Denn gerade weil Du dies bisweilen versäumst und Deine Meinung mit derben, oft feindselig aussehenden Worten aussprichst, so kann Niemand wissen, wie eigentlich Deine persönlichen Gesinnungen für den, gegen welchen Du Dich aussprichst, beschaffen sind, ob Du ihn achtest oder verachtest, ob Du seine sonstigen Verdienste anerkennst oder als Dreck betrachtest. Lichtenberg sagt irgendwo: 'Da, wo man sonst Einem eine Ohrfeige gab, sagt man jetzt, erlauben Sie gütigst.' Es wird doch verschieden aufgenommen, ob man Jemandem sagt: Du hast eine Dummheit gemacht, Du bist ein Esel, oder ob man sagt: Ich bin anderer Meinung und glaube, die Sache verhält sich so und so."

In 1840 Liebig began to give his attention to physiology and agriculture. April 2, 1840, he writes: "Du weisst, ich schreibe soeben eine närrische Chemie, die es mit der Physiologie und dem Ackerbau zu thun hat. Was werden die Leute für Augen machen, dass ein Chemiker sich herausnimmt zu behaupten, die Physiologen und Agronomen seien die unwissendsten Pfuscher!" Soon afterwards the celebrated article "Ueber den Zustand der Chemie in Preussen" was written. In regard to this Liebig writes: "Hätte ich es mit Dir und zwei oder drei Anderen zu thun gehabt, so wäre vieles überflüssig gewesen; allein mein Zweck ist, auf das grosse Publicum und auf die Regierungen zu wirken. Der Himmel gebe seinen Segen dazu und emancipiere uns. Die Chemie stand bisher, den anderen Fächern gegenüber, in einer sonderbaren Lage, wir werden gewissermassen als Eindringlinge betrachtet; allein dies soll sich ändern, sie soll neben oder über den anderen stehen." Liebig is now tired of laboratory work, and in 1841 he writes: "Die Lust am Laboriren verliert sich später, wir haben genug laborirt, und ich bin es ungeheuer müde. Alle diese Specialitäten interessiren mich nicht mehr, nur die Anwendungen reizen mich, und dies muss Gegenstand der späteren Lebensperiode werden." October 22, 1843, he writes again: "Ich bin jetzt in Verlegenheit über Aufgaben und Fragen zu Arbeiten und verwünsche oft das ganze Laboratorium; ich tröste mich nur, dass es Dir auch so geht." That Wöhler at times felt the same appears in several letters. Thus on January 24, 1845, he writes: "Die Schulmeisterei bin ich herzlich satt, auch das Prakticum langweilt mich *souverainement.*" And again, in December of the same year: "Das verdammte Prakticum hat mich bis jetzt so sehr in Anspruch genommen, dass ich alles darüber versäume und vergesse. Lange kann man es wirklich nicht mehr aushalten, oder, was ebenso schlimm ist, man lässt die Sache ins Liederliche ausarten und muss dann sagen hören: es geht mit ihm bergab."

Liebig's investigation on creatine acquires a new interest when we read under date December 18, 1846: "Ich habe jetzt einen alten, mageren Gaul verarbeitet und hoffe so viel Kreatin zu bekommen, dass ich die Untersuchung beendigen kann." Wöhler's reply is characteristic in its humor: "Ich sehe im Geist die übelriechenden Kochereien die Du jetzt in Deinem Laboratorium vornehmen und rieche die Pferdefleischsuppen, die Du kochen lässest. Eine colossale Idee, einen ganzen Gaul zur Kreatin-Bereitung zu verwenden. Ich gratulire zu der neuen Frau Base. Das sind ja wunderbare Dinge."

Immediately after the death of Berzelius Liebig writes: "Ich bin entschlossen, mit Kopp und Andern künftig einen Jahresbericht herauszugeben, wenn auch nur deswegen, um denselben nicht in andere und schlechtere Hände fallen zu lassen."

The troubles of 1848 and 1849 led Liebig to think of a solution of the problem as far as he and Wöhler were concerned, which might have had an incalculable influence on this country. On May 29 he writes: "Wird es auf der andern Seite ebenso schlimm, und ist ein Blutbad unvermeidlich, so gehen wir Alle nach Amerika und gründen dort eine deutsche Universität."

In 1852 Liebig accepted a call to Munich, one of the conditions being that he should not be obliged to teach in the laboratory, and, further, the number of lectures he was to give was small. "Ich werde im Sommer wöchentlich nur zweimal (je 1½ St.) lesen; ich nehme Prakticanten an, die aber an mich nichts bezahlen, so dass ich in dieser Hinsicht nicht gebunden bin." Later he writes: "Ich nehme keine Eleven in mein Laboratorium auf mit der Verpflichtung, sie zu unterrichten; aber ich will einer Anzahl von jungen Männern erlauben, in meinem Laboratorium zu arbeiten und die Hülfsmittel zu benützen, die es darbietet, ohne jedoch dass sie irgend Ansprüche wegen Aufgabe oder Leitung einer Arbeit an mich machen dürfen. So viel es mir bequem ist, werde ich mich immer mit ihnen beschäftigen, aber nicht mehr. Theurer Freund, Du wirst mich verstehen; ich habe 28 Jahre lang diesen Karren in dem Dreck gezogen, und es fehlt mir die Kraft, es ferner zu thun. Wenn ich irgend noch thätig sein will, so muss ich mich beschränken. Ich fühle, wie wohl es mir ist, dieser Qual ledig zu sein; seit Jahren war ich nicht so gesund als diesen Winter, bloss weil ich weniger meinen Kopf anzustrengen hatte. Auch bei Dir wird die Zeit kommen, und ich wünsche Dir Glück dazu, wenn Du die Gelegenheit hast Dich loszuschälen. Wir haben unser Leben lang geschafft und gearbeitet genug, Keiner, ich sage mit Wahrheit, Keiner wird es uns nachmachen."

From this time on Liebig gave but little attention to pure chemistry. Wöhler, however, though frequently complaining, continued to occupy himself in the laboratory and, as is well known, with brilliant results. In 1856 he fears that he will not be able to give practical instruction during the coming winter. Organic chemistry, which owes so much to the two masters, is rapidly growing away from them. Liebig does not profess to know much about it; and in 1859 Wöhler writes: "Morgen beginnt wieder meine Qual, das Prakticum, und morgen in acht Tagen die Vorlesung. Die organische Chemie ist jetzt wahrhaft zum Verzweifeln, es wird Einem übel, wenn man manche Abhandlung liest; dennoch hätte ich Lust, einen Griff darin zu thun; doch man muss nicht von ungelegten Eiern reden." In 1865 he writes: "Ich glaube es ist Zeit, die Chemie aufzugeben und Gärtner oder Eisenbahnschaffner zu werden." And a little later: "Lieber Freund, mir geht es wie Dir, die Laboratoriumsatmosphäre ist mir höchst zuwider, der Anblick eines Glases voll Salpetersäure macht mir fast übel; um die Details der organischen Chemie bekümmere ich mich fast gar nicht, das Meiste, was das junge Epigonengeschlecht macht, besteht doch eigentlich in der Ausfüllung der Maschen eines Stickmusters. Ich weiss dass ich übertreibe, und verkenne nicht, wohin diese zahllosen Arbeiten am Ende führen können. Das Einzige, was mir noch Befriedigung gewährt sind meine Vorlesungen, weil ich nun nach vierzigjähriger Uebung zu wissen glaube wie und was man vortragen soll."

In 1867 both were growing out of patience with the methods of instruction then in vogue in the laboratories. Liebig writes: "Diese Leute verstehen ganz gut eine organische Analyse zu machen, sonst aber verstehen sie nichts von der praktischen Chemie. In der Kunst Präparate darzustellen, sind sie in der Regel ganz ungeübt, sie haben keine Freude daran, sie halten es für Zeitverlust, da man heute alle Sachen in den chemischen Fabriken kaufen kann. Das chemische Studium wird in den modernen Laboratorien immer einseitiger, und die Leute für die Praxis immer unbrauchbarer. An Chemikern, die eine gute Mineralanalyse machen können, ist ein solcher Mangel, dass ich mich jetzt vergeblich nach einem umgesehen habe." To this Wöhler replies: "Was Du über das moderne Studium der Chemie sagst, ist mir ganz aus der Seele geschrieben. Meinetwegen, ich lasse sie laufen; sie haben keine Freude und Lust mehr an den Dingen, sie wollen nur rechnen und formeln."

On December 31, 1871, Liebig writes as follows: "Lange werden wir uns Glückwünsche zu neuen Jahren nicht mehr senden können; aber auch wenn wir todt und längst verwest sind, werden die Bande, die uns im Leben vereinigten uns Beide in der Erinnerung der Menschen stets zusammenhalten, als ein nicht häufiges Beispiel von zwei Männern, die treu, ohne Neid und Missgunst, in demselben Gebiete rangen und stritten und stets in Freundschaft eng verbunden blieben."

Liebig's last letter to Wöhler was written April 3, 1873. He died April 18. Wöhler survived him ten years, his death having occurred September 23, 1883.

It would be an easy matter to quote many more interesting passages from the letters. Indeed there is scarcely a page in the two volumes that will not be read with interest. In closing this inadequate notice no more appropriate words can be used than those placed by Wöhler himself on the bundle containing the correspondence between him and Liebig:

> "Seh' ich die Werke der Meister an,
> So seh' ich das, was sie gethan;
> Betracht' ich meine Siebensachen,
> Seh' ich, was ich hätt' sollen machen."—GOETHE.

I. R.

INVESTIGATIONS ON THE TERPENES AND ETHEREAL OILS.

The terpenes have long been the subject of chemical investigation, but until quite recently the results have not been satisfactory. The statement is generally made that a large number of isomeric hydrocarbons of the formula $C_{10}H_{16}$ are known, but these have not been sharply characterised, and it has been a matter of doubt as to how many of the terpenes which have been described under different names are distinct chemical individuals, and the constitution even of the best-studied members of the group has not been determined with any certainty. During the last few years Professor O. Wallach, of Bonn (since called to Göttingen), has been engaged in the investigation of the terpenes and ethereal oils, and other related compounds, and he has thrown a great deal of light upon the chemistry of these compounds. It is the purpose of this paper to give a brief account of the results obtained in Professor Wallach's investigations as far as they have been described.

In the first paper,[1] which is by O. Wallach and W. Brass, an account of an investigation of worm-seed oil (*Oleum Cynæ*) is given. It is found that this oil consists essentially of an oxygen compound of the formula $C_{10}H_{18}O$, which, as it is isomeric with borneol, the authors call *cineol.* This combines with hydrochloric acid, forming the compound $(C_{10}H_{18}O)_2HCl$. When the hydrochlorate is heated, it undergoes decomposition in accordance with the following equation:

$$(C_{10}H_{18}O)_2HCl = 2H_2O + HCl + 2C_{10}H_{16}.$$

By conducting hydrochloric acid gas into worm-seed oil while heated, the hydrocarbon $C_{10}H_{16}$ is readily formed.

Hydriodic acid acts upon cineol thus:

$$C_{10}H_{18}O + 2HI = H_2O + C_{10}H_{18}I_2.$$

When bromine and cineol are brought together in the cold in petroleum ether, they unite to form the compound $C_{10}H_{18}O.Br_2$. If this is left undisturbed in a sealed tube in a cool place, it yields a crystallised compound, $C_{10}H_{16}Br_4$, which is formed also by the action of bromine on the hydrocarbon $C_{10}H_{16}$:

$$(C_{10}H_{18}O)Br_2 = H_2O + C_{10}H_{16} + Br_2;$$
$$C_{10}H_{16} + 2Br_2 = C_{10}H_{16}Br_4.$$

The tetrabromine addition-product melts at 125.5°. The authors call the hydrocarbon, $C_{10}H_{16}$, obtained from cineol, *cinene.* It is obtained most readily by heating the iodide, $C_{10}H_{18}I_2$, in aniline:

$$C_{10}H_{18}I_2 + 2C_6H_5NH_2 = C_{10}H_{16} + 2C_6H_5NH_3I.$$

Concentrated sulphuric acid converts cinene into cymene; as does also phosphorus pentasulphide.

Having found that at least one of the terpenes can be sharply characterised by chemical reactions, an investigation of terpenes in general suggests itself.[2] The first result is to show that the oxygen compound contained in cajeput oil, and hitherto known as cajeputol, is identical with cineol. It is found further that the hydrocarbon $C_{10}H_{16}$, obtained from *oleum corticis auriantorum*, and known as *hesperidene*, is not identical with cinene, as it yields a tetrabromide which melts at 104°–105°. There are then at least two distinct tetrabromides which can be obtained from terpenes, and which can be easily recognised. With this knowledge Wallach proceeds to examine a large number of ethereal oils, and the results obtained may be summed up in these words:[3]

(1). Those terpenes which are obtained from orange-peel oil, lemon oil, oil of bergamot, oil of caraway, dill oil, erigeron oil, and pine-needle oil, are identical. This hydrocarbon is the *hesperidene* above referred to. It yields a tetrabromide melting at 104°–105°, and is thus easily recognised.

(2). The terpenes boiling between 180° and 182°, and known as cinene, cajeputene, caoutchene, diisoprene; that portion of the oil of camphor which boils between 180° and 182°; the product obtained by heating terpenes to 250°–270°; and finally the hydrocarbons obtained by decomposition of the terpene dichlorhydrate $C_{10}H_{16}.2HCl$, melting at 49°–50°, no matter what the source may be—all the above are identical. They yield the tetrabromide melting at 125°.

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[1] Annalen der Chemie **225**, 291 (1884). [2] Ibid. **225**, 314. [3] Ibid. **227**, 297.

Whether all the very similar terpenes boiling at about 160°, which are found in oil of turpentine, pine-needle oil, juniper oil, lemon oil, eucalyptus oil, mace oil, dill oil, sage oil, etc., are identical or not cannot be positively stated as yet. It is, however, certain that they are all converted into the same hydrocarbon at higher temperatures.

In investigating the products formed in the destructive distillation of caoutchouc, the author readily obtained two, viz. *caoutchene* and *isoprene*. The former is unquestionably identical with cinene. Isoprene boils at 34°–39°. While heated alone it is polymerised, yielding caoutchene or cinene. It follows from this that some of the terpenes bear to the pentenes C_5H_8, the same relation that diamylene bears to amylene.

The author now proposes the following classification of the terpenes:

A. HEMITERPENES OR PENTENES OF THE FORMULA C_5H_8.

Examples: Isoprene and valerylene.

B. TERPENES PROPER, $C_{10}H_{16}$.

These fall into several groups, each of which is composed of several members:

1. *Pinene Group.*

These boil at about 160°; give bromine addition-products which are liquid; nitroso-derivatives melt at 129°; combine with one molecule hydrochloric acid to form saturated compounds. By heat and acids they are converted into other groups.

Examples: Terebentene, australene.

2. *Camphene Group.*

These are solid; melt at about 50°, and boil at about 160°. Their conduct towards bromine is yet to be investigated.

3. *Limonene Group.*

Boiling point between 175°–177°; have characteristic odor of lemons; nitroso-derivative melts at 71°; bromine addition-product melts at 104°–105°; addition-product with hydrochloric acid ($+ 2HCl$) melts at 50°, and is identical with dipentene dihydrochlorate; converted into dipentene by heat.

Examples: Hesperidene, citrene, carvene. These are identical and are called *limonene.*

4. *Dipentene Group.*

Boiling point 180°–182°; odor like that of limonene; tetrabromide melts at 125°; takes up two molecules of hydrochloric acid, forming a compound which melts at 49°–50°; at high temperature undergoes polymerisation without previous conversion into another modification.

Examples: Diisoprene, cinene, cajeputene, caoutchene, isoterebentene. These are identical and are called *dipentene.*

C. POLYTERPENES, $(C_5H_8)x$.

Some of these occur ready formed in nature, while others are formed by polymerisation of hemiterpenes and terpenes. But little is known in regard to them.

1. *Sesquiterpenes or Tripentenes*, $C_{15}H_{24}$.

Boiling point 250°–260°.
Examples: Cedrene, cubebene, etc.

2. *Diterpenes or Tetrapentenes*, $C_{20}H_{32}$.

Boiling point above 300°.
Example: Colophene.

3. *Polyterpenes*, $(C_{10}H_{16})_x$.

Example: Caoutchouc.

A thorough examination of Russian and Swedish oil of turpentine[1] shows that these consist essentially of pinene, sylvestrene, and dipentene, the most characteristic constituent being sylvestrene. When this is treated with hydrochloric acid in ethereal solution it yields a hydrochlorate melting at 72°. It is shown, further, that terpine hydrate is a saturated compound. When it is boiled with acids or with dehydrating agents, the first product formed is terpineol, $C_{10}H_{18}O$, and by further dehydration three different hydrocarbons are formed according to the conditions. These are *terpinene*, *terpinolene*, and *dipentene*. Terpineol is an unsaturated monatomic alcohol. Next a pure *sesquiterpene*,[2] which is found in cubeb oil, oil of patchouly, galbanum oil, and abundantly in juniper oil (*oleum cadinum*) and sabine oil (*oleum sabinæ*), is thoroughly studied.

In the fifth paper Wallach[3] states that it is now possible sharply to characterise eight hydrocarbons, $C_{10}H_{16}$, so that it is not difficult to recognise them. These are: Pinene, camphene, limonene, dipentene, terpinolene, sylvestrene, terpinene, and phellandrene.

1. *Pinene*, and 2. *Camphene*.—When cold pinene is saturated with hydrochloric acid, a compound of the formula $C_{10}H_{16}.HCl$ is formed. This can be distilled almost without decomposition.

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[1] Annalen der Chemie **230**, 225 (1885). [2] Ibid. **238**, 78 (1887). [3] Ibid. **239**, 1 (1887).

It acts like a saturated compound. When the hydrochlorate is heated to 200° with sodium acetate and glacial acetic acid, it is converted into camphene. Pinene can be converted also into dipentene by heating the free hydrocarbon; by the action of moist hydrochloric acid; by the action of dilute nitric or sulphuric acid. On the other hand, dilute sulphuric acid, which so easily transforms pinene, acts very slowly upon camphene. The atoms in the molecule of camphene are apparently in a condition of more stable equilibrium than the atoms in the molecule of pinene.

3. *Limonene.*—This is strongly dextro-rotary. It forms a tetrabromide melting at 104°–105°. This also is dextro-rotary. With hydrochloric, hydrobromic, and hydriodic acids it forms compounds of the formulas $C_{10}H_{16}.2HCl$ (m. p. 50°), $C_{10}H_{16}.2HBr$ (m. p. 64°), and $C_{10}H_{16}.2HI$ (m. p. 77°–79°). These compounds are optically inactive and are derivatives of dipentene.

4. *Dipentene.*—This is formed by superheating isoprene, pinene, and limonene, and is therefore found in all those terpene oils in the preparation of which a high temperature is used, as, for example, the Russian and Swedish oils of turpentine, and in caoutchene. It is formed also by the action of sulphuric acid on pinene; by the dehydration of terpine hydrate, terpineol, and cineol; by the action of hydrochloric acid on pinene and limonene; by the action of the same acid on terpine hydrate, terpineol, and cineol. Dipentene and all its derivatives are optically inactive. Its most characteristic derivatives are the tetrabromide (m. p. 125°); the dihydrochlorate, $C_{10}H_{16}.2HCl$ (m. p. 50°); the dihydrobromate, $C_{10}H_{16}.2HBr$ (m. p. 64°); the hydriodate, $C_{10}H_{16}.2HI$ (m. p. 77°–79°). It is easily converted into terpinene by sulphuric or hydrochloric acid.

5. *Terpinolene.*—This hydrocarbon is formed by boiling terpine hydrate, terpineol, or cineol with dilute sulphuric acid, and by the inversion of pinene with sulphuric acid. Its boiling point lies between 185° and 190°. Its tetrabromide melts at 116° when perfectly pure. The solutions of the tetrabromide are optically active. It appears that terpinolene, like limonene, is converted into dipentene by treatment with the halhydric acids. Terpinolene is certainly one of the most changeable terpenes.

6. *Sylvestrene.*—This is most readily obtained from Swedish oil of turpentine. It boils at 175°–178°. When heated to 250° in sealed tubes it is partly polymerised, but apparently it is not converted into an isomeric modification. It is one of the most stable of the terpenes. It is dextro-rotary. The hydrochlorate $C_{10}H_{16}2HCl$ melts at 72°, and its solutions are dextro-rotary; the hydrobromate $C_{10}H_{16}2HBr$ also melts at 72°. The tetrabromide $C_{10}H_{16}Br_4$ melts at 135°–136°, and its solution in ether is dextro-rotary.

7. *Terpinene.*—This is obtained together with other substances by heating terpine hydrate with dilute sulphuric acid, and by the inversion of pinene with alcoholic sulphuric acid. It is formed, further, when oil of turpentine (pinene) is shaken with concentrated

sulphuric acid, if care is taken to prevent too great a rise of temperature. It is easily recognised by the aid of its nitrite $C_{10}H_{16}N_2O_3$, which is made by bringing it together with acetic acid and a water solution of sodium nitrite. The nitrite crystallises well and melts at 155°. With the halhydric acids terpinene gives only liquid products. Terpinene is not easily converted into another terpene by the action of sulphuric acid, and is one of the stable terpenes.

8. *Phellandrene.*—This hydrocarbon occurs in water fennel oil (*Phellandrium aquaticum*) and in bitter fennel oil. It was discovered by Cahours in the former and afterwards found by Pesci in the latter. It is easily recognised by the aid of its nitrite, which melts at 94°. The oils containing phellandrene are strongly dextrorotary, while the nitrite of the hydrocarbon is levo-rotary. A solution of the nitrite in chloroform does not take up bromine, its conduct being like that of a saturated compound. It is difficult to obtain phellandrene in pure condition, and it is certain that it is one of the most changeable terpenes. Treatment with hydrobromic acid in solution in glacial acetic acid converts it into dipentene. When heated for a few hours with alcoholic sulphuric acid it is converted into terpinene.

The eight modifications of terpene which are certainly known can be grouped in three classes.

A. The members of the first class combine with one molecule of hydrochloric acid, and have, therefore, but one double bond between carbon atoms.

B. The members of the second class combine with two molecules of hydrochloric acid, and have, therefore, two double bonds between carbon atoms.

C. The members of the third class are distinguished by their power to form addition-products with nitrogen trioxide. These compounds are formed in cases in which an aromatic substance contains an unsaturated paraffin residue.

The terpenes of the first class (A) are pinene and camphene.

Those of the second class (B) are limonene, dipentene, sylvestrene, and terpinolene.

Those of the third class (C) are phellandrene and terpinene.

The easy formation of the addition-products with nitrogen trioxide leads next to a more careful study of the reaction involved, and the results obtained are described in four papers. These results will be presented in a connected way below, as some of them are only indirectly related to the chief problem under discussion.

The next paper[1] bearing upon the relations between the terpenes is the eighth in the series. This is of special importance. The author's latest investigations have shown that the pine-needle oils contain limonene, but not the ordinary variety. Ordinary limonene is dextro-rotary, while that contained in the pine-needle oils is levo-rotary. The tetrabromide melts at 104°, as does that from ordinary dextro-limonene. It crystallises in the same forms with the same angles, *but with opposite hemihedral faces.* The solution of the tetrabromide of levo-limonene is levo-rotary, and the solution of the tetrabromide of dextro-limonene is dextro-rotary. It appears, therefore, that dextro-limonene and levo-limonene are chemically identical, but physically isomeric hydrocarbons. Of great interest is the fact that *when the dextro- and levo-limonenes are mixed in equal quantities, dipentene is formed.* When such a mixture is treated with bromine, the tetrabromide, melting at 124°–125°, is formed, whereas each of the limonenes gives the bromide melting at 104°–105°. Further, when the dextro-rotary tetrabromide and the levo-rotary tetrabromide are mixed, the tetrabromide melting at 124°–125° is formed.

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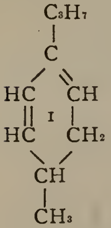
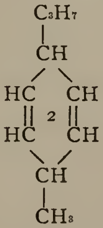
[1] Annalen der Chemie **246**, 221 (1888).

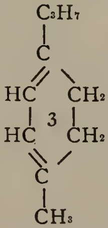
The above relations are strongly suggestive of those which exist between dextro- and levo-tartaric acids and racemic acid.

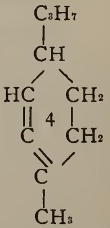
Just as two varieties of limonene have been found, so the author has also found two varieties of phellandrene. That variety which occurs in elemi oil is dextro-rotary, while that which occurs in eucalyptus oil is levo-rotary. The nitrite of dextro-phellandrene is levo-rotary, and that of levo-phellandrene is dextro-rotary. When the two active nitrites are mixed together, an inactive nitrite is formed. It has not yet been determined what hydrocarbon is formed by mixing dextro- and levo-phellandrene.

It is an easy matter to devise structural formulas which will account for the facts thus far established. It appears that some of the terpenes, those which take up two molecules of hydrochloric acid, and therefore probably have two double carbon bonds, are true hydrocymenes. For these a large number of formulas are possible according to the theory. The following may serve as examples:









etc.

A compound of formula 1 should be optically active; one of formula 2 inactive. The same would be true of their bromine addition-products, while it is clear that two molecules of hydrochloric acid could be added to 1 and to 2 in such ways as to give identical inactive compounds. The author, however, wisely restrains from premature speculation on the subject, as he is convinced that the facts known are not sufficient to justify a conclusion in regard to the constitution of any one of the terpenes.

In the eleventh paper in the series[1] some new relations between the derivatives of dipentene are discussed. It has already been shown that when dextro-limonene and levo-limonene are mixed, dipentene is formed. The relations between the two optically active varieties of limonene and inactive dipentene are like those between dextro- and levo-tartaric acids and racemic acid. But, as is well known, there is an inactive tartaric acid, and the question will suggest itself whether there is a second variety of dipentene. Investigation shows that there is. Levo-limonene was converted into the nitroso-chloride, when it was found that the product consisted of two isomeric varieties (α- and β-), both of which are levorotary. So also dextro-limonene yields two isomeric nitrosochlorides (α- and β-) both of which are dextro-rotary. When these nitroso-chlorides are treated with bases, as aniline, piperidine, etc., each one gives a different base with the same optical activity as the nitroso-chloride from which it is formed. Thus:

+ Limonene gives + α-Base and + β-Base;
— Limonene gives — α-Base and — β-Base.

Further, when + α-Base and — α-Base are mixed, they give a new base which is inactive; and + β-Base and — β-Base also give a new base which is inactive. These two new bases are derivatives of dipentene, and a mixture of the two is obtained when dipentene is taken as the starting point. The relations existing between these various compounds is shown by the table below:

+ Limonene and — Limonene give Dipentene.
+ Limonene yields $\left\{\begin{array}{l} (1) + \alpha\text{-Base.} \\ (2) + \beta\text{-Base.} \end{array}\right.$
— Limonene yields $\left\{\begin{array}{l} (3) - \alpha\text{-Base.} \\ (4) - \beta\text{-Base.} \end{array}\right.$
+ α-Base and — α-Base give (5) α-Base (inactive).
+ β-Base and — β-Base give (6) β-Base (inactive).

Dipentene yields α-Base (inactive) and β-Base (inactive). Starting with dipentene, therefore, it is possible theoretically to obtain through the nitroso-chloride six different bases.

On the Nitrosates and Nitrosites.—As it has been shown that some of the terpenes have the power to combine with oxides of nitrogen, while others have not, and that this power is clearly connected with the presence of unsaturated paraffin residues, an investigation of some of the compounds thus formed is taken up. In a paper[2] entitled "Ueber Nitrosate und Nitrosite sowie über einige aus denselben darstellbare neue Verbindungen," the chief results described are as follows: The addition of the trioxide N_2O_3, and of the tetroxide of nitrogen, N_2O_4, does not always take place in the same way. The differences appear to be due for the most part to the structure of the compounds used. The compound formed by the addition of nitrogen tetroxide to amylene may serve as the representative of a large group of compounds. This substance is not a nitro-compound nor a dinitrite, $C_5H_{10}(NO_2)_2$, but it contains a nitrate group, $-O(NO_2)$, and a nitroso or isonitroso group, so that it may properly be called a *nitrosonitrate* or, better, a *nitrosate*. Some compounds formed by the addition of nitrogen trioxide to hydrocarbons are perfectly analogous to the nitrosates, but they contain a nitrite group, $-O(NO)$, instead of the nitrate group, and they may therefore be called *nitrosonitrites* or *nitrosites*. Both the nitrosates and the nitrosites undergo chemical change very readily, exchanging the nitrate or the nitrite group for other constituents with the greatest ease. With bases products are formed which contain the group NH_2, NHR or NR_2. These the author calls *nitrolamines*. Assuming that the nitrosate contains the isonitroso group, the change with aniline is represented thus:

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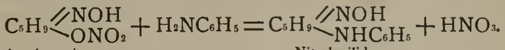
[1] Annalen der Chemie **252**, 106 (1889).

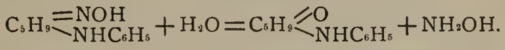
[2] Ibid. **241**, 288 (1887).



$$C_5H_9\begin{array}{l}/\!\!/NOH\\ \diagdown ONO_2\end{array} + H_2NC_6H_5 = C_5H_9\begin{array}{l}/\!\!/NOH\\ \diagdown NHC_6H_5\end{array} + HNO_3.$$

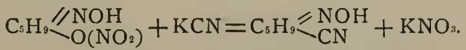
Amylene-nitrosate. Nitrolanilide.

When the hydrochloric acid compound of the anilide is boiled with water or concentrated hydrochloric acid, the isonitroso group is replaced by oxygen, hydroxylamine being formed at the same time, as in the case of the acetoximes and ketoximes:



$$C_5H_9\begin{array}{l}=NOH\\ \diagdown NHC_6H_5\end{array} + H_2O = C_5H_9\begin{array}{l}/\!\!/O\\ \diagdown NHC_6H_5\end{array} + NH_2OH.$$

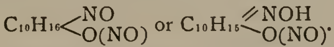
The nitrosates act also upon potassium cyanide as represented in this equation:



$$C_5H_9\begin{array}{l}/\!\!/NOH\\ \diagdown O(NO_2)\end{array} + KCN = C_5H_9\begin{array}{l}/\!\!/NOH\\ \diagdown CN\end{array} + KNO_3.$$

Nitrosites of the formula $R\begin{array}{l}\diagup NOH\\ \diagdown ONO\end{array}$ exist. With a mixture of nitrogen trioxide and the tetroxide, sometimes a nitrosate is formed and sometimes a nitrosite, according to the properties of the product.

In a later paper[1] an account is given of a nitrosite obtained from terpinene which must be represented by the formula



$$C_{10}H_{16}\begin{array}{l}\diagup NO\\ \diagdown O(NO)\end{array} \text{ or } C_{10}H_{15}\begin{array}{l}/\!\!/NOH\\ \diagdown O(NO)\end{array}.$$

According to observations made by Maissen and confirmed by Wallach, limonene yields a nitrosate. According to the above, it is probable that some of the terpenes contain unsaturated paraffin residues. Finally, a still later paper[2] in the series treats more in detail of amylene nitrosate and compounds derived from it. The object of the investigation is to determine from which amylene the nitrosate is derived. It is certain that not all unsaturated hydrocarbons yield nitrosates. Caprylene, for example, does not yield one, and the different amylenes conduct themselves differently towards the oxides of nitrogen. Amylene nitrosate is easily obtained from commercial amylene, boiling at 36°–38°. The nitrosate was first treated with potassium cyanide, and a nitrile thus formed:

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[1] Annalen der Chemie **241**, 315 (1887).

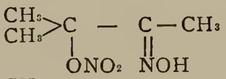
[2] Ibid. **248**, 161 (1888).

$$C_5H_{10}.NO.NO_3 + KCN = KNO_3 + C_5H_{10}.NO.CN.$$

When the nitrile is boiled with caustic potash it yields colorless needles,

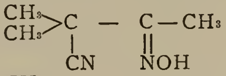
$$C_5H_{10}NO.CN + H_2O = C_5H_{10}.NO.CONH_2,$$

and the potassium salt of an acid of the formula $C_5H_{10}NO.COOH$ is formed at the same time. When heated above its melting point this acid loses carbon dioxide, and a liquid of the composition $C_5H_{11}NO$ is formed. This is the hydroxylamine derivative of methyl-isopropyl ketone, as was proved by making the compound directly from the ketone. The relations between the compounds mentioned are shown by the following formulas:



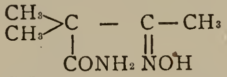
$$\mathrm{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle ONO_2}{\underset{|}{C}} - \underset{\displaystyle NOH}{\underset{\|}{C}} - CH_3}$$

Nitrosate;



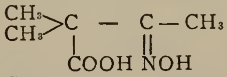
$$\mathrm{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle CN}{\underset{|}{C}} - \underset{\displaystyle NOH}{\underset{\|}{C}} - CH_3}$$

Nitrile;



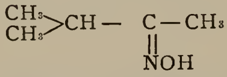
$$\mathrm{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle CONH_2}{\underset{|}{C}} - \underset{\displaystyle NOH}{\underset{\|}{C}} - CH_3}$$

Amide;



$$\mathrm{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle COOH}{\underset{|}{C}} - \underset{\displaystyle NOH}{\underset{\|}{C}} - CH_3}$$

Acid;



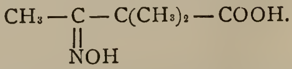
$$\mathrm{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH - \underset{\displaystyle NOH}{\underset{\|}{C}} - CH_3}$$

Ketoxime;

The acid obtained from amylene by the method described is the hydroxylamine derivative of dimethylacetoacetic acid, as appears from the following formulas:

$$CH_3 - CO - C(CH_3)_2 - COOH;$$

Dimethylacetoacetic acid.



$$\mathrm{CH_3 - \underset{\displaystyle NOH}{\underset{\|}{C}} - C(CH_3)_2 - COOH.}$$

The author proposes to call all acids which contain the group $-C(NOH)-CH_3$ *ketoxime acids.* Hence, the above acid is called *ketoxime-dimethylacetoacetic acid.*

The amylene used in these experiments may be either trimethylethylene, $(H_3C)_2C{=}CH(CH_3)$, or isopropylethylene, $(H_3C)_2CH-CH{=}CH_2$. If, however, it could be conclusively shown that the ketoxime acid obtained is ketoxime-dimethylacetoacetic acid, the proof that amylene is trimethylethylene would be complete. This was shown by making ethyl dimethylacetoacetate, saponifying, and treating with hydroxylamine, when the same acid was obtained as that above described. From this it follows that the amylene from which the nitrosate is derived is trimethylethylene. It appears probable, from the evidence thus far obtained, that nitrosates can be obtained from those unsaturated hydrocarbons which are trisubstitution products of ethylene. It remains to be determined how the disubstituted ethylenes $R_2C{=}CH_2$ and $RHC{=}CHR$ will conduct themselves.

The investigation on the terpenes is still in progress.

I. R.

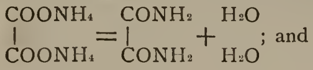
GESCHICHTE DER CHEMIE VON DEN ÄLTESTEN ZEITEN BIS ZUR GEGENWART. ZUGLEICH EINFÜHRUNG IN DAS STUDIUM DER CHEMIE. Von Dr. ERNST VON MEYER, a. o. Professor an der Universität Leipzig. Leipzig: Veit & Comp., 1889. 466 pp. 8vo.

The author of this book has endeavored to furnish a *short* history of the development of chemical knowledge from the beginning to the present day. His work differs, therefore, markedly from Kopp's *Geschichte*, which is not short, and from Ladenburg's *Entwickelungsgeschichte*, which begins with Lavoisier. The book is clearly written, and it is evident that the author has to a considerable extent formed his own judgment in regard to the important movements. As regards the older periods, the treatment is in the main in accordance with that of other historians. Indeed, writers generally have relied upon Kopp for the early history of chemistry, and one scarcely looks for novelty of treatment in this part of the subject. For the majority of students who want to get a general idea concerning the early history of chemistry the book is well adapted.

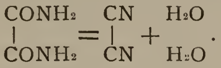
In dealing with the work of Lavoisier the author plainly shows that his mental equilibrium has been somewhat disturbed by Würtz's unfortunate, famous phrase: "La chimie est une science française; elle fut constituée par Lavoisier," etc. He agrees with Volhard that Lavoisier was rather a physicist than a chemist, while at the same time he acknowledges the great influence of this remarkable man. He says (p. 129): "Die grosse That Lavoisier's bestand in der Abstreifung alter Vorurteile und in der mustergültigen Anwendung wissenschaftlicher Prinzipien bei der Erklärung chemischer Vorgänge. Ein reiches Material von wichtigen Thatsachen war ihm von den Phlogistikern überliefert; er selbst hat dieses durch neue Beobachtungen, was die *chemische*

Seite derselben anlangt, um wenig bereichert, wohl aber dasselbe von einem bis dahin unerreichten Standpunkte aus zu sichten und zusammenzufassen vermocht, sowie für viele Vorgänge die richtige Erklärung gegeben. Man wird nicht fehlgehen, wenn man solche Leistungen auf Rechnung seines physikalisch und mathematisch vorzüglich geschulten Geistes setzt, welcher schon frühzeitig von den Fesseln der phlogistischen Hypothese frei zu machen wusste. Als *Physiker* musste sich Lavoisier vor allen Dingen Rechenschaft geben von Gewichtsveränderungen, z. B. bei der Verkalkung von Metallen; die Eigenschaften der Produkte interessierten ihn weniger. Daraus erklärt es sich, dass er selbständige *chemische* Entdeckungen nicht gemacht hat; sein Verdienst, die Beobachtungen anderer zuerst umfassend und richtig gedeutet zu haben, bleibt darum unbestritten." It is a little difficult to understand the distinction made by Volhard and Von Meyer. It would seem that one who by the aid of his own experiments furnishes an entirely satisfactory explanation of all the phenomena of combustion must be familiar with a large number of chemical facts, must be able to grasp the great problems of chemistry, must be able to think chemically, must in short be a chemist. It matters little, however, what he is called. If the discussion is of any value, it is for the reason that it furnishes an admonition to chemists to study physics. Avogadro and Dalton were fortunately not chemists in the usual sense of the word. "Selbständige chemische Entdeckungen" are not the only things of importance for chemistry.

The influence of the researches of Würtz, Hofmann, and Williamson on the development of the theory of types is discussed very satisfactorily, so that the reader can see clearly how these researches must have worked on the minds of cotemporaneous chemists. Unquestionably the work on the substituted ammonias was of the highest importance in impressing upon chemists the reality of the view according to which these compounds are derived from ammonia by the substitution of one, two, or three of the hydrogen atoms by radicals. It was these experiments which enabled chemists to decide in favor of the typical view as against the view that the compounds are "*copulated.*" There is especially one experiment of Hofmann which is almost crucial. As this, so far as the writer of this notice is aware, is not given its full due in works on the history of chemistry, a few words regarding it will not be out of place here. The question under discussion was simply this: In an ammonia-base, like aniline, is ammonia present as such, copulated with a radical as represented in the formula $C_6H_4 \supset NH_3$, or is one of the hydrogen atoms of the ammonia replaced by a radical as represented in the formula $C_6H_5.NH_2$? The former was the view commonly held in accordance with the theory of copulated compounds; the latter view had been put forward by Liebig, and was known as the amide theory. In working on the derivatives of aniline, Hofmann showed that the conduct of aniline oxalate, under the influence of dehydrating agents, can be accounted for only by the aid of the amide theory. As is well known, when ammonium oxalate is dehydrated, two stages are observed. These are represented by the equations

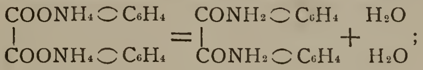


$$\begin{array}{l}COONH_4\\ |\\ COONH_4\end{array} = \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} + \begin{array}{l}H_2O\\ \\ H_2O\end{array}\text{; and}$$

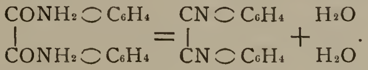


$$\begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} = \begin{array}{l}CN\\ |\\ CN\end{array} + \begin{array}{l}H_2O\\ \\ H_2O\end{array}.$$

Now, if aniline is a copulated compound and contains ammonia, then aniline oxalate ought to undergo two similar changes:

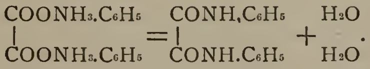


$$\begin{array}{l}COONH_4 \supset C_6H_4\\ |\\ COONH_4 \supset C_6H_4\end{array} = \begin{array}{l}CONH_2 \supset C_6H_4\\ |\\ CONH_2 \supset C_6H_4\end{array} + \begin{array}{l}H_2O\\ \\ H_2O\end{array};$$



$$\begin{array}{l}CONH_2 \supset C_6H_4\\ |\\ CONH_2 \supset C_6H_4\end{array} = \begin{array}{l}CN \supset C_6H_4\\ |\\ CN \supset C_6H_4\end{array} + \begin{array}{l}H_2O\\ \\ H_2O\end{array}.$$

But the second change cannot be effected. It therefore appears improbable that ammonia, as such, is present in aniline. If, on the other hand, it is assumed that aniline is a substituted ammonia, the fact that the second change of the oxalate cannot be effected is easily understood. The following equation expresses the first change:



$$\begin{array}{l}COONH_3.C_6H_5\\ |\\ COONH_3.C_6H_5\end{array} = \begin{array}{l}CONH.C_6H_5\\ |\\ CONH.C_6H_5\end{array} + \begin{array}{l}H_2O\\ \\ H_2O\end{array}.$$

And it will be seen that the second change cannot take place without involving the hydrogen atoms of the radical. As the above facts lead to the amide theory, so the subsequent preparation of a number of the ammonia-bases from ammonia and halogen compounds of the alkyls "konnte als ein trefflicher Beweis für die Richtigkeit der Annahme gelten, dass diese Körper aus Ammoniak durch Austausch eines oder mehrerer Wasserstoffatome gegen Alkoholradikale hervorgegangen sein" (p. 240).

Due credit is given Sterry Hunt for his part in the development of the theory of types. On p. 243 we find this passage: "Eine grössere Ausdehnung gab dieser typischen Auffassung seit dem Jahre 1848 der amerikanische Chemiker Sterry Hunt, welcher in mehreren Abhandlungen die Ableitung zahlreicher sauerstoffhaltiger Körper, unorganischer sowie organischer, von dem Wasser, die der Kohlenwasserstoffe von dem Typus Wasserstoff lehrte. Da seine Erörterungen in Europa kaum bekannt wurden, so haben dieselben auch keinerlei beschleunigenden Einfluss auf die Entwickelung der ähnlichen in manchen Köpfen vorhandenen Anschauungsweise ausgeübt."

In the passage from the type theory to the valence hypothesis the chief credit is justly given to Frankland, though the influence of Kolbe is by no means forgotten. Concerning these two chemists and their work the author says (p. 259): "Diese beiden Männer, die originellsten Forscher auf dem Gebiete der organischen Chemie in jener Sturm- und Drangperiode der fünfziger Jahre, haben durch ihr Wirken ganz wesentlich dazu beigetragen, dass die Eigentümlichkeit der Gerhardt'schen Typen als beruhend auf der verschiedenen Sättigungskapazität der in denselben enthaltenen Grundstoffe erkannt wurde. Das Hauptverdienst in dieser Richtung gewirkt zu haben, fällt Frankland zu." In order that full justice may be done, a section of the book bears the title, "Begründung der Lehre von der Sättigungskapazität der Grundstoffe durch Frankland."

In discussing Kekulé's memoir, "Ueber die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," the author says (p. 266): "Der Gedankengang ist fast der gleiche, welchen Frankland zur Ableitung der Drei- und Fünfwertigkeit des Stickstoffs, Phosphors, Arsens und Antimons führte. . . . . Daraus ergiebt sich aber, dass in jenem Ausspruch Kekulé's nicht eine durchaus originelle Leistung oder eine wissenschaftliche That erblickt werden kann, umsoweniger, als die Vierwertigkeit des Kohlenstoffs sowohl von Frankland, wie von Kolbe schon erkannt war, und namentlich den Erörterungen des letzteren über die Konstitution organischer Verbindungen zu Grunde lag. . . . Kekulé's Verdienst in dieser Angelegenheit muss darin gesucht werden, dass er der Frage nach der Art, wie sich zwei und mehr Kohlenstoffatome mit einander verbinden und ihre Affinitäten sättigen auf den Grund zu gehen suchte. Das unmittelbare Ergebnis dieser Spekulationen ist die Lehre von der Verkettung der Atome in den chemischen Verbindungen gewesen. Mittelbar haben die Ansichten Kolbe's und Frankland's an der Entwickelung dieser in der Strukturtheorie gipfelnden Betrachtungsweise den wesentlichsten Antheil gehabt."

It appears clear that chemists generally have erred in ascribing the valence hypothesis solely to Kekulé. Kekulé himself, in his memoir, says that the views put forward by him are not his own, but that they are applications of views previously expressed by others. At the same time it would not be just to fly to the other extreme, as Von Meyer seems inclined to do. While it cannot be denied that Frankland first clearly recognised the saturating power of the elements and that his work on this subject had the highest value, it must also be acknowledged that Kekulé's work exerted a powerful influence in leading chemists to recognise the truth of the new conception.

The last part of the book (pp. 300–449) has the title: "Spezielle Geschichte einzelner Theile der Chemie seit Lavoisier bis auf die

Gegenwart." The subjects treated under this general head are as follows: Geschichte der analytischen Chemie; Spezielle Geschichte der unorganischen Chemie; Specielle Geschichte der organischen Chemie im 19. Jahrhunderte; Geschichte der physikalischen Chemie in der neueren Zeit; Zur Geschichte der mineralogischen Chemie während der letzten hundert Jahre; Entwickelung der Agrikulturchemie und der physiologischen Chemie; Geschichte der technischen Chemie in den letzten hundert Jahren; Zur Entwickelung des chemischen Unterrichts im 19. Jahrhundert, namentlich in Deutschland.

The section on physical chemistry gives, in the space of twenty-seven pages, a clear account of the recent developments of this subject.

One word in regard to the title of the book. The words "Zugleich Einführung in das Studium der Chemie" are misleading. Nothing is more certain than that the history of chemistry is entirely meaningless to one who has not studied chemistry pretty thoroughly. Only the mature chemist, who by long study has become familiar with chemical changes and chemical substances, can profit by the study of the history of the science. For such a one the study is of great value and, indeed, essential if he is to understand the present views and to estimate their value fairly. As a guide to the study, Professor Von Meyer's book can be cordially recommended to advanced students. As far as possible, the original articles which are referred to should also be studied with care. Of course, in the time at the disposal of a student, only a comparatively small number of these classical articles can be thoroughly studied, but a beginning can at least be made, and a clear understanding of one brief period will be of great assistance in enabling the student to understand the whole subject. Then, too, it is well to bear in mind that the most profitable study is that which is done after the so-called student-years are over.

I. R.

FORTSCHRITTE DER THEERFARBENFABRIKATION UND VERWANDTER INDUSTRIEZWEIGE 1877–1887. AN DER HAND DER SYSTEMATISCH GEORDNETEN UND MIT KRITISCHEN ANMERKUNGEN VERSEHENEN DEUTSCHEN REICHS-PATENTE. Dargestellt von Dr. P. FRIEDLÄNDER, Privatdocent an der technischen Hochschule zu Karlsruhe i. B. Berlin: Springer. 1888.

Those who are interested in the manufacture of coal-tar dyes will welcome this book; and even scientific chemists who have no connection with patents will find much to interest them in it, for in the laboratories of the dye-factories, observations are constantly made, and most of these are lost to the outside chemical world. The author has had several years' experience on the technical side, and is thus able to give a great deal of information not usually given in books on this subject, and in cases in which his own observations were not sufficient he has called in the aid of others. The results of his labors are given in a book of 614 pages 4to. No attempt can be made to review the book as a whole, but some idea of its extent may be gained by the statement that 94 pages are devoted to tri-phenylmethane dyes; 31 pages to indigo-blue, isatin, and indol derivatives; 71 pages to quinoline, quinoxaline, phenylpyrazol, and pyrrol compounds; and 214 pages to azo-dyes.

In the chapter on indigo we learn that of all the patents taken out bearing upon the artificial preparation of indigo, only two have any industrial importance. These are (1) that for the preparation of *o*-nitrophenyl-propiolic acid; and (2) that covering the fixing of indigo on the fiber by means of *o*-nitrophenyl-propiolic acid and xanthogenates. But the demand for the acid remains very small. Of the large number of quinoline derivatives, methods for the preparation of which have been patented, only three are of importance from a technical point of view. These are quinaldine, thalline, and kairine. The members of the pyrazol group, which are made by the action of primary hydrazines with β-diketo compounds, are of importance on account of their physiological action. As is well known, that one which is most extensively used is antipyrine.

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A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

BY WOLCOTT GIBBS, M. D., *Rumford Professor (Emeritus) in Harvard University*, AND H. A. HARE, M. D., *Demonstrator of Therapeutics and Instructor in Physical Diagnosis in the Medical Department and in Physiology in the Biological Department of the University of Pennsylvania.*

The investigation which we have undertaken has for its object to determine whether it is possible to trace general laws in the action of definitely related compounds upon the animal organization, so that it may be possible to predict, within certain limits at least, what the action of a given substance will be, and what modifications that action will undergo when chemical changes are produced by the replacement of particular elements or groups of elements, or by other definite and generally applicable chemical processes. We hope to be able to offer at least a contribution toward an answer to these questions.

A certain amount of work in this direction has already been done, the results of which we shall cite in their proper places; but as far as we know, nothing approaching a thorough systematic study of the subject has yet been attempted.[1]

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[1] See for instances: Brown, A. C., and T. R. Fraser, "On the changes produced by direct chemical addition on the physiological action of certain poisons." Proc. Roy. Soc. Edinb., 1866–9, **6**, 228.

Brown, A. C., and T. R. Fraser, "On the connection between chemical constitution and

The number of questions which arise is of course very great, and the varying conditions both chemical and physiological are very numerous. Even a partial solution of the problem which we have proposed can hardly fail, however, to afford valuable materials for the formation of a system of rational therapeutics.

The plan which we have laid out for our work embraces the following special subjects of study:

1. Related substances belonging to the aromatic series. These offer by far the widest and richest field for study, in consequence of the multiplicity of possible combinations. Thus, to cite a few cases, we have:

a. The comparison of homologous series, as for instance nitro-benzol, the nitro-toluols, etc.

b. The comparison of the properties of ortho, meta and para compounds.

c. The effect of successive replacements of hydrogen by the same molecule, as for example in nitro-phenol, $C_6H_4NO_2OH$, dinitro-phenol $C_6H_3(NO_2)_2OH$, and trinitro-phenol $C_6H_2(NO_2)_3OH$, or again in the case of phenol C_6H_5OH, pyrocatechin o.$C_6H_4(OH)_2$, resorcin m.$C_6H_4(OH)_2$, and hydroquinone p.$C_6H_4(OH)_2$, and finally pyrogallol and phloroglucin $C_6H_3(OH)_3$.

2. Primary alcohols of the series $CRH_2.OH$.

3. Secondary alcohols of the series CR_2HOH.

4. Tertiary alcohols of the series CR_3OH.

5. The amides of the fatty acids beginning with formamide and corresponding anilids.

6. Hydrazines or bodies derived from N_2H_4 by more or less complete replacement of hydrogen.

7. Nitroso-compounds, as for instance nitro-methane.

8. Hyponitrites.

To these we propose to add such others as the progress of our investigation may show to possess special interest. The instances cited will be sufficient to illustrate the general scope and purpose of our work. We have commenced with the study of the relative

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physiological action; on the physiological action of the salts of ammonia, of tri-methylamine, and tetramethylammonium" [etc.], *Ibid.* p. 556.

Brown, A. C., and T. R. Fraser, "On the connection between chemical constitution and physiological action, with special reference to the physiological action of the salts of the ammonium bases derived from strychnia, brucia, thebaia, codeia, morphia, and nicotia." Jour. Anat. and Physiol., London, 1868, **2**, pp. 224–242. [Index Catalogue, 1888, **9**, p. 62.]

Also, "Contributions to our knowledge of the connexion between chemical constitution, physiological action and antagonism." By T. Lauder Brunton, M. D., F. R. S., and J. Theodore Cash, M. D. Philosophical Transactions of the Royal Society, Part I, 1884.

action of certain ortho, meta and para compounds, very beautiful preparations of which we owe to the kindness of Prof. Ira Remsen.

To prevent misunderstanding, it may be well to state in this place that Dr. Gibbs is responsible for the plan, general conduct and purely chemical portions of this memoir. The whole of the experimental work has been executed by Dr. Hare. In the discussion of the results of the investigation both will take part. The physiological work was performed in the laboratory of Experimental Therapeutics of the University of Pennsylvania.

NITROPHENOLS.

Ortho-nitro-phenol.

On the normal dog ortho-nitro-phenol has no apparent effect, as far as the eye can discern, when injected into the jugular vein in the proportion of from 0.002 gram to 0.016 gram to the kilo, nor does this amount affect normal bodily temperature.

Upon the pyrexia produced by cocaine ortho-nitro-phenol evidently acts with some power.

In every one of eight experiments the temperature fell several degrees in from one to two hours, but no marked fall occurred in less than one hour, and we are therefore unable to state positively that the fall of temperature when it did occur was due to the drug or to the fact that the cocaine had largely been eliminated by that time and as a consequence no longer produced fever. This will have to be studied by means of "pepsin fever," which is of longer duration. The doses given to the fevered dogs ranged from 0.002 gram to 0.016 gram per kilo.

On the heart ortho-nitro-phenol has by no means as depressing an influence as its sister, the meta compound; enormous doses rapidly given by the jugular vein being required to produce death, more than 0.1 gram for every kilo. If given by the jugular vein to a dog of 10 kilos in a dose of 0.075 gram the pulse becomes slower, owing to stimulation of the inhibitory apparatus, both peripheral and centric.

Death is produced by cardiac, not respiratory failure, as the animal continues to breathe for some moments after cardiac arrest.

Meta-nitro-phenol.

In three experiments upon dogs this compound exercised no appreciable influence, although the drug was given hypodermically and the animals were closely watched for as long as six hours and a half. The doses were 0.013 gram to the kilo in one case, in another case 0.044 to the kilo, and in the third 0.072 gram to the kilo.

As regards the effect of meta-nitro-phenol on normal temperature we found that it possesses no power, although the compound was given intravenously, the jugular vein being used. The dose was 0.0033 gram to the kilo.

The influence of the compound on the fevered animal is as yet not positively decided, although we believe that but a few more experiments are necessary to decide this point. In two of the four experiments made by us the thermo-genetic agent was cocaine, and in these meta-nitro-phenol failed to cause a fall. In the remaining two animals in which pepsin was used to produce the fever this compound produced a fall of temperature equal to 2°.1 Fahr. in one case in 50 minutes, while in the second case the fall was 0°.7 Fahr. in 35 minutes. In the two cocainised animals the dose of the drug was 0.005 gram to the kilo and 0.071 gram to the kilo respectively, while in the pepsinised dogs it was 0.0625 gram to the kilo and 0.018 gram to the kilo.

We believe that the explanation of these apparently contradictory effects is very readily reached, not by the variation in dosage, for in the cocainised dog one of the doses was larger than that given to either pepsinised animal, but in the fact that cocaine produces such a violent storm of fever heat as to sweep all things before it unless they are very powerful in their anti-pyretic influence. Thus we have seen 0.062 gram of cocaine given by the jugular vein raise the rectal temperature of a large dog 6° Fahr. in less than an hour.

Further experiments are therefore necessary before we can consider meta-nitro-phenol as an anti-pyretic of reliability.

It should be remembered that all the studies made in this paper on bodily temperature, unless otherwise stated, were made upon animals free to run about.

On the circulatory system we find that when as much as 0.5 gram of the drug is injected rapidly into the jugular vein of a dog of 6 kilos, death occurs immediately from heart failure due to a direct depressant influence on this viscus. If smaller amounts be given the pulse is slowed by as much as 20 beats per minute, this slowing being caused first by centric, then by a peripheral stimulation of the inhibitory nervous apparatus governing the heart. The drug, however, cannot be considered in any way dangerous to the heart when taken by the stomach.

Para-nitro-phenol.

When this drug is given hypodermically to dogs in the proportion of from 0.011 gram to 0.020 gram to the kilo it produces absolutely no effect as far as can be seen.

On the normal temperature, as taken in the rectum, the drug given in the dose of from .0025 to .003 gram to the kilo raises the bodily temperature from 1°.3 Fahr. to 1°.8 Fahr., the animal being free to run about. The influence of this compound upon the temperature of fevered animals we have not yet studied.

When as much as 0.01 gram to the kilo of para-nitro-phenol is injected very rapidly into the jugular vein of a dog, death immediately occurs by cardiac arrest, not of inhibitory origin, for paralysis of these nerves in no way influences the result.

If on the other hand the injection is very slow indeed, so that but small amounts reach the heart at once, only slight and temporary cardiac depression results. After the lapse of ten minutes the pulse becomes very rapid, while the blood pressure, now no longer depressed, rises to the normal or above it. We have proved that this rapidity of circulation is due to a palsy of the peripheral inhibitory nerves of the heart. Half an hour later the pulse becomes slower by ten to twelve beats per minute, and simultaneously there is a fall of arterial pressure, evidently due to an action on the vaso-motor system, since asphyxia at this time produces no rise.

From these results on the higher animals it is evident that the nitro-phenols are possessed of little power over the nervous system, and our studies upon the frog have proved this conclusion to be correct. Indeed, we do not think that we have ever seen any substances which affect the heart so powerfully as do these agents and yet influence the nervous system so imperceptibly.

Ortho-nitro-phenol, the least poisonous of these substances, when given in the dose of .001 gram to the gram of frog seems to exert no perceptible influence on the nervous system, and even the heart is not sufficiently involved to give rise to much general disturbance. When as much as 0.0032 gram to the gram is used, slight evidences of weakness show themselves.

When meta-nitro-phenol is injected into the posterior lymph-sac in the dose of 0.0015 gram to the gram of the frog, no symptoms appear for some minutes. After the lapse of half an hour, however, the animal becomes relaxed and inactive, though the muscles and nerve trunks react well to galvanic stimulus. That there is no impairment of function in the nerves or muscles is proved by the fact that if one limb is protected from the poison, the unprotected nerves and muscles respond equally well to stimulation, and that the spinal cord is unaffected is proved by the fact that reflexes are preserved till death. The heart invariably stops in diastole, the ventricle being full of blood. In one experiment in which the dose was 0.009 gram to the gram of frog, marked dicrotism of the heart was noted.

In our studies of para-nitro-phenol, which it will be remembered was the most lethal of the group in mammalia, we find that when .020 gram of the compound is injected into the posterior lymph-sac of a frog weighing 40 grams, the batrachian immediately becomes relaxed and torpid and in less than five minutes dies from cardiac failure, the heart stopping in diastole with an engorged ventricle. The fatal result is so rapid in its onset and the heart is so evidently affected from the first that we believe the partial lack of response to peripheral irritation which occurs at this time to be solely due to approaching death, since repeated experiment has shown that the nerve trunk and muscles when stimulated with electricity respond perfectly.

Summary.

The lethal doses of the phenols in the dog are as follows:

Ortho-nitro-phenol produces death when only .1 gram is given for each kilo.

Meta-nitro-phenol when given in the dose of a little more than 0.1 gram to each kilo. To every three kilos it will not produce death.

Para-nitro-phenol produces death when as much as 0.01 gram to the kilo is given by the jugular.

The toxicity of these compounds is therefore as follows: para, the most poisonous; meta the next; ortho the least. We shall discuss the subject more fully hereafter.

All the nitro-phenols produce death by paralysing the heart, and not by a respiratory action.

They have very little effect over bodily heat even in fever, the meta compound seeming to be the most powerful in this action. Curiously enough, the ortho and meta compounds stimulate the vagus nerves, while the para compound appears to depress them. On the nervous system their action is probably indirect and is certainly very slight indeed.

It has been noted that every animal killed by the use of the phenols, or after the injection of a less than lethal dose, putrifies rapidly, becoming intensely swollen, while other animals killed by other means and lying in the same vault suffered as yet no change.

NITRANILINES.

Ortho-nitraniline.

When 0.5 gram of ortho-nitraniline is administered by the mouth to dogs of from 4 to 10 kilos, no symptoms appear for about ten minutes; after the lapse of which, violent sneezing comes on, the animal sneezing once a minute on the average. Five minutes later these paroxysms become so severe that the head is struck against the floor with each expiratory movement. There is no evidence of nasal irritation, save pawing at the nose at rare intervals, no increase of secretion save the moisture driven out by the drafts of air. The sneezing lasts about forty minutes, then ceases entirely and is followed by no signs of depression. The animal seems as well as ever and remains so indefinitely. Four hours after the dose has been given, a single attack of vomiting with the expulsion of a little watery fluid may occur.

When as much as 0.01 gram to the kilo is injected into the jugular vein of a dog, the blood pressure falls temporarily, but instantly rises again to a point above that occupied before, equalling 16 mm. The pulse rate remains about the same for about seven minutes, then becomes slower by many beats; this is probably due to certain struggling respiratory movements which occur at this time, as it does not occur in the curarised animal. Ten minutes later the pulse rapidly becomes slower, dropping in five minutes from 186 to 90 per minute, and in the course of one minute more to 60. Section of the vagi at this time causes a very slight increase in rate, which, of course, points to stimulation of these nerves peripherally. Here again this apparent action is proven a real one by the fact that if atropine is now given in large enough dose to paralyse the vagus, the pulse immediately becomes rapid, reaching 174 beats per minute.

The lethal dose of this compound is 0.30 gram to the kilo; 0.15 will not kill when given by the jugular. After death from the drug the blood is found dark and grumous looking, and the spectroscope shows the presence of methaemoglobin.

When 0.043 gram of ortho-nitraniline is injected into the posterior lymph-sac of a frog weighing 32 grams, there is some irritation produced by the acid required to dissolve the compound. Three minutes after the injection the reflexes are found to be intact, but the respirations are noted as having ceased, so far as the movement of the throat and sides is concerned. Following this the reflexes appear to fail quite rapidly and relaxation of a marked type comes on. Irritation of the foot fails to call forth any drawing away of that member, but the tremors of the muscles of the thigh show that the sensory impulse travels upwards at least to some extent. Later, however, sensation is completely lost, for burning of the foot causes no withdrawal, although motion is fairly well preserved. That this loss of sensation is due to an action on the spinal cord, on its sensory side, is proved by the fact that if a ligature is placed around the blood-vessels of a limb and the drug injected below the ligature, this failure of sensation does not occur.

Quite early in the poisoning the heart becomes very much slower than before, finally beating only 24 beats a minute. Its movements at this time are also very feeble; indeed, the circulation at this period is so much impaired that we believe that the symptoms noted are largely due to failure of this part of the organism. Finally, after progressive failure the heart stops in wide diastole.

Meta-nitraniline.

Meta-nitraniline, when injected into the jugular vein of a dog weighing 7 kilos in the dose of 0.5 to 0.8 gram, causes no appreciable fall of pressure, but a very marked slowing of the pulse, amounting to as much as forty beats a minute; slowing which we have proved to be in part due to peripheral "vagal" stimulation, for section of these nerves causes by no means as great an increase of rate as is normal. The slowing cannot be due to an action on the heart, for there is, as already stated, no change in pressure or in pulse force.

When 0.085 gram of meta-nitraniline is given to a frog weighing 25 grams hypodermically, in eight minutes the respirations become somewhat increased in number, and reflex action is also rendered more excitable. This condition lasts for some minutes, and is succeeded by a return to the normal state or one of reduced reflex activity. Five minutes later the reflexes become markedly lessened, and at this time the frog will remain on his back when so placed.

The respirations, which before the dose of the poison were 44, now change to 54. No further change in the reflexes occurs, and it is also to be remarked that the muscles and nerves still respond to electrical stimuli with apparently their normal tone. The spinal cord also responds readily to stimuli. It is evident that the compound has little influence over the nervous system of the frog, except very indirectly. If the substance is given to the dog or rabbit by the mouth, in a short time the animal passes into a condition of quietude and lies down in a state bordering on sleep, if the dose has been as much as 0.10 gram to the kilo or 0.30 gram to the kilo.

In our belief, these symptoms are all due to the influence which the compound exercises on the blood, and spectroscopic examination of this fluid shows the presence of methaemoglobin. This view is also supported by the results reached in the frog, for in these animals there was no direct involvement of the nervous system, but an evident indirect action of the compound. The symptoms produced are also remarkably like those of ordinary aniline poisoning, for there is profuse salivation, total loss of muscle tone, and so great an amount of relaxation that it is difficult to distinguish it from palsy. The reflexes of the eyelids are perfectly preserved, showing that general paralysis is not present.

Para-nitraniline.

The effects of para-nitraniline are much more marked and severe than are those of ortho- or meta-nitraniline. Given to a dog of 4½ kilos in the dose of 0.5 gram, in thirty minutes the springy gait is lost and an unsteadiness in movement is noted, the head is held high in air, and a peculiar guttural note is given forth. Later he staggers as if drunk, the saliva forms from the mouth, and urine is passed of a greenish yellow color. The retching and vomiting upsets the equilibrium of the animal and he falls, and in an hour passes into apparent unconsciousness, but the eye reflexes are perfectly intact. A curious paroxysm of Cheyne Stopes, breathing and barking, comes on every five minutes by the clock and lasts sixty seconds. Running movements accompany the yelps as the animal lies on its side. Death occurs in coma three hours after the administration of the dose.

When para-nitraniline is injected into the jugular vein of a dog, in the dose of 0.003 gram to the kilo, in the space of 70 seconds it produces a slight fall of arterial pressure and pulse rate, the slowing of the latter becoming more and more marked until the decrease from the original rate equals 50 beats a minute. That the fall of blood pressure is rather the result of momentary disturbance caused by the injection than any special action, is proved by the fact that asphyxia instantly causes a rise. These same changes occurred in another instance where the dose was 0.002 to the kilo.

That the slowing of the pulse is due to a stimulation of the peripheral vagi is proved by the fact that section of these nerves causes almost no increase in pulse rate, and also because at this time the tracing showed no evidence of cardiac depression.

In experiment No. 3, where but 0.0007 gram was given to each kilo, no change of any moment occurred save that when the vagi were cut the pulse failed to increase its rate as it should do in the normal animal. In experiment No. 4 0.033 gram to each kilo was injected in divided doses, but no other changes than those already noted.

That the slowing of the pulse is due to peripheral vagal stimulation is proved by the fact that atropine injected into the circulation prevents this change in the pulse when para-nitraniline is given. The fatal dose of this compound when injected into the jugular is .040 gram to the kilo.

Summary.

The lethal dose of ortho-nitraniline is about 0.3 gram to the kilo of animal. It slows the pulse by stimulating the peripheral vagi and produces methaemoglobin in the blood. The action on the nervous system consists chiefly in an effect on the sensory side of the cord, but probably depends on the changes in the blood, and is slight and indirect. In large amount the drug is a powerful cardiac depressant.

The sneezing produced by it when given by the stomach is the most curious symptom produced.

Meta-nitraniline also stimulates the peripheral vagi, thereby slowing the pulse. The nervous effects are very feeble and depend upon the changes in the blood, namely, the development of methaemoglobin, all the symptoms being those of aniline poisoning.

Para-nitraniline is by far the most poisonous member of the group, and acts like the other members in a stimulating manner on the peripheral vagi.

The lethal dose of it is 0.04 gram to the kilo by the jugular vein.

AMIDO-BENZOIC ACIDS.

The Amido-benzoic Acid Group.

With a few exceptions it may be stated that this class of substances are without any effect upon the animal organism. Whether they are given to animals by the stomach or intravenously, the normal condition of the system remains unchanged in its functional activity.

Ortho-amido-benzoic Acid.

The administration of 2 grams of this substance for every 8 kilos of dog's weight was entirely without effect.

Profuse urination occurred in one instance, given below, six minutes after the ingestion of the dose, and could not therefore have been due to the action of the drug.

Dog weight, 8 kilos; 3.25, rectal temperature 103.2.

3.32, 2 grams of drug by oesophageal tube in 40 cc. aq.

3.38, has urinated profusely.

3.40, has defecated loosely.

4.25, no other symptoms; rectal temperature 103.

The next day the animal was perfectly well.

On the circulation the results are almost equally barren. After the injection of 1 gram for every 6 kilos by the jugular vein, no symptoms appear for about 9 minutes, when a decided slowing of the pulse occurs. As this occurs both in curarised and non-curarised animals, it must depend on some direct effect of the drug. Further experimentation has shown that the inhibitory nerves are stimulated centrically and peripherally, since under these circumstances section of these nerves causes slight increase in rate not equal to that occurring in the normal dog, a fact which points to peripheral inhibitory stimulation. This peripheral action would seem proved, since atropine failed to produce an increase in rate when ortho-amido-benzoic acid was given first.

Meta-amido-benzoic Acid.

This compound also has no influence over the animal economy, as will be seen in the following examples of some of the experiments in which no change in bodily temperature or general condition occurred:

Dog weight, 4 kilos; 12.26, rectal temperature 103.
12.28, 1 gram of compound in 40 cc. aq.
12.31, vomited 10 cc. of dose.
1.40, no symptoms; rectal temperature 102.8.
2.30, no symptoms; rectal temperature .

Dog weight, 5 kilos: 12.30, rectal temperature 99.5.
12.22, 2 grams of compound in 40 cc. aq.
12.50, vomited about 10 cc.
1.40, no symptoms; rectal temperature 100.
2.30, no symptoms.

Careful manometrical studies of the circulatory apparatus after doses of the compound by the jugular vein give results identical with those already given, and even so much as 1 gram to every 5 kilos of the dog's weight produces no influence. In one experiment in which the entire mass of the injection (1 gram in 40 cc. aq.) was sent *en masse* into the heart, there was for a moment a fall of blood pressure of about 20 millimeters of mercury, which lasted for only 10 seconds, and was dependent on the rapidity of the injection.

When para-amido-benzoic acid is given by the stomach to a dog, so that for each 7 kilos of the animal 500 milligrams of the drug are used, nothing occurs, and this is likewise true when such a large dose as 2 grams to every 5 kilos are employed; in one case slight vomiting came on, but as a very small amount of liquid was ejected, none of the drug was lost, and it is probable that the efforts at vomiting were largely volitional and due to the irritation of the fauces by the oesophageal tube used when giving the dose. No fall in the normal bodily temperature occurred, as was proved by the insertion of a rectal thermometer before and after dosage.

Urination came on one hour after the dose was given, but the quantity passed was small in amount and probably had no dependence on the drug. The two following experiments give results similar to those found in all the others:

Dog weight, 7 kilos; 11.30, rectal temperature 102.1.

11.35, 500 milligrams of drug by oesophageal tube in 60 cc. of water.

1.05, no symptoms whatever so far.

2.05, no symptoms whatever so far.

Next day, no symptoms as yet.

Dog weight, 5 kilos; 12, rectal temperature 102.5.

12.02, 2 grams of drug as before.

12.15, vomited about 5 cc. of liquid, but no drug.

12.35, rectal temperature 102.5.

1.40, rectal temperature 102.5; no symptoms whatever so far.

1.45, urinating slightly, about 60 cc.

On the circulation, as studied by the mercurial manometer, this compound gives results of no more importance than those already stated. The pulse rate and arterial pressure undergo no changes when doses of from 500 milligrams to 1 gram to every 8 kilos of the dog's weight are given by the jugular vein in the space of 10 seconds in 30 cc. of sodium carbonate solution.

NITRO-BENZOIC ACIDS.

Ortho-nitro-benzoic acid when injected into the jugular vein of the dog, or when given by the stomach, in the dose of 1 gram to every 4 or 5 kilos, seems to have very little, if any, influence over the animal free to run about, only a very slight relaxation of the general system being evidenced by a desire to keep quiet. That this tendency to be quiet and still is rather the result of the operation of opening the jugular vein, or forcing the drug into the stomach, is proved by the fact that the animal walks without difficulty and responds to caresses.

It is to be noted, too, that the symptoms of depression, such as they are, are in part due to the use of a saturated solution of sodic carbonate as a solvent of the drug. That such a solvent is in no way injurious to the compound itself is well known, as the salts of the blood change all such acids into sodic salts as soon as they enter the circulation. The bodily temperature remains unaffected.

If ortho-nitro-benzoic acid is injected by the jugular vein in the same dose as just mentioned (1 gram to every 4 or 5 kilos), there are no changes of note in the arterial pressure or pulse rate, even though the solution is concentrated and rapidly injected.

Given to the frog hypodermically it seems equally innocuous, and we therefore have reached the conclusion that this compound is a substance possessing almost no influence over the body in ordinary amounts.

Meta-nitro-benzoic Acid.—If this compound is injected into the jugular vein or stomach of an animal free to move about, in the dose of from 0.25 gram to 1 gram to every 7 kilos, no more symptoms ensue than follow the use of the preceding salt.

Correspondingly we find that the circulatory apparatus remains unaffected, and that both the pulse rate and arterial pressure are undisturbed, and it is therefore almost inert physiologically in the doses named.

Para-nitro-benzoic Acid has also an equally feeble influence, and the entire group seems to be alike in its harmlessness.

(*To be continued.*)

ON PENTAMIDOBENZOL.[1]

By A. W. Palmer and C. Loring Jackson.

Nearly two years ago, in a paper upon Tribromtrinitrobenzol,[2] one of us in conjunction with J. F. Wing described some attempts to reduce triamidotrinitrobenzol, and announced that the work would be continued. Before doing this, however, it seemed advisable to try similar experiments with the triamidodinitrobenzol, as this substance can be obtained much more easily, and the experience gained in this way would be useful when we returned to the much less accessible trinitro compound. Accordingly, we have undertaken together the work on the dinitro compound, which has led, as we had hoped, to the preparation of the chloride of pentamidobenzol; but, shortly after we had sent to the *Berichte der deutschen chemischen Gesellschaft* a preliminary notice[1] of this substance, a number of the same journal reached us containing a paper by Andrew Barr[2] in which the chloride of pentamidobenzol was also described, and, as this paper, although it came into our hands after our preliminary notice had been sent, was presented to the German Chemical Society a fortnight before ours was written, we have dropped this line of work in order to avoid interfering with Barr, or Merz, in whose laboratory the research of Barr was carried on, and publish in this paper the results which had been already obtained by us when we received Barr's paper. The method of making pentamidobenzol used by us is different from that of Barr, who prepared the diamidotrinitrobenzol from the ethylether of trinitroresorcine and alcoholic ammonia, and then reduced this product with tin and hydrochloric acid, whereas we submitted to a similar reduction the triamidodinitrobenzol made by the action of alcoholic ammonia on tribromdinitrobenzol. Both this triamido and the corresponding trianilido compound are new, and an account of them is therefore included in this paper.

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[1] From the Proceedings of the American Academy of Arts and Sciences, communicated by the authors.

[2] This Journal **10**, 283 (1888).

Triamidodinitrobenzol, $C_6H(NH_2)_3(NO_2)_2$.

This substance was prepared by treating tribromdinitrobenzol,[3] melting point 192°, with alcoholic ammonia; but this action takes place much less easily than in the case of the corresponding trinitro compound, for whereas that was attacked by alcoholic ammonia in the cold, and the reaction was rendered complete by short boiling in a flask with a return condenser, the dinitro compound gave no action with alcoholic ammonia in open vessels, but it was necessary to heat the two substances under pressure in the water-bath to bring about the reaction.

As we had no digester fit for this purpose, we were obliged to heat the mixture in soda-water bottles, which were kept in a boiling water-bath for about eight hours. The contents of the bottles at the end of this time consisted principally of a mixture of dark reddish yellow needles with nearly black amorphous masses. There was also a colored alcoholic solution, which on evaporation left a red amorphous substance with a comparatively low melting point; but this was formed in such small quantities that we did not attempt to study it beyond ascertaining the fact that it is not altered by further heating with alcoholic ammonia. The tribromtrinitrobenzol, when treated with alcoholic ammonia, forms a similar by-product,[1] soluble in alcohol, which is now under investigation. The two products of the reaction which were not dissolved in the alcohol were separated mechanically, washed thoroughly with various solvents, and analysed without further purification, as they both showed such a slight solubility in all the common solvents that a crystallisation of them in any quantity was a matter of very great difficulty. In spite of the great difference in their appearance they both had the same composition, that of the expected triamidodinitrobenzol, as is shown by the following analytical data, in which Analyses I and II were made with the reddish yellow needles, Analysis III with the black amorphous body.

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[1] Ber. d. chem. Gesell. **21**, 1706 (1888).

[2] Ib. **21**, 1541 (1888).

[3] The tribrombenzol used in making this substance must be purified by crystallisation from alcohol after it has been distilled, as, if this crystallisation is omitted, a substance melting in the neighborhood of 95° remains mixed with the tribrombenzol, and gives rise to very impure products after the treatment with nitric acid. The nature of this impurity will be considered in another paper.

I. 0.3000 gram of the substance crystallised in yellow needles gave on combustion 0.3710 gram of carbonic dioxide and 0.1085 gram of water.

II. 0.1510 gram of the crystalline substance like that used in I gave 42.4 cc. of nitrogen at a temperature of 8.6° and a pressure of 748.5 mm.

III. 0.3028 gram of the substance deposited in black amorphous masses gave on combustion 0.3778 gram of carbonic dioxide and 0.0925 gram of water.

	Calculated for $C_6H(NH_2)_3(NO_2)_2$.	Found. I.	II.	III.
Carbon	33.80	33.73	...	34.02
Hydrogen	3.28	4.02	...	3.39
Nitrogen	32.87	...	33.31	...

Properties.—The triamidodinitrobenzol, as deposited by the action of alcoholic ammonia on tribromdinitrobenzol, forms either reddish yellow needles, or nearly black amorphous masses. When the substance is crystallised from a mixture of chloroform and alcohol, which can be done only with great difficulty on account of its slight solubility, it forms microscopic yellow plates, or broad flattened prisms, and, if the treatment with the mixed solvents is carried on in a continuous extracter, these crystals collect into characteristic yellow masses shaped like an S or U. It does not melt even above 300°, but is decomposed if heated more intensely. It is very slightly soluble in alcohol or chloroform, although it imparts a perceptible yellow color to these solvents; more soluble in nitrobenzol, but cannot be obtained in crystals easily from this solution, so that a mixture of alcohol and chloroform is the best solvent for it. In the other common solvents it is either entirely insoluble or very slightly soluble. In this respect it resembles the corresponding trinitro compound, but it is, if there is any difference, slightly more soluble than that. The substance does not form definite salts, although it dissolves easily in concentrated hydrochloric acid, forming a dark red liquid. It shows therefore a greater tendency to form salts than the triamidotrinitrobenzol, which is insoluble in strong hydrochloric acid.

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[1] This Journal **10**, 290.

Trichloride of Pentamidobenzol, $C_6H(NH_2)_2(NH_3Cl)_3$.

To prepare this substance, some of the triamidodinitrobenzol (either the crystalline or amorphous) was heated on the water-bath in a flask with strong hydrochloric acid, a very strong solution of stannous chloride, granulated tin, and some pieces of platinum foil. After some hours the very deep red solution had lost most of its color, but still showed a dirty brownish yellow tint; it was then allowed to cool, when crystals were deposited, which increased in quantity, if the liquid was saturated with hydrochloric acid gas. The crystals were filtered out, and washed with concentrated hydrochloric acid, then, as we did not succeed in removing the salts of tin completely by precipitation from an aqueous solution with hydrochloric acid gas,[1] the substance was dissolved in very little water and the solution saturated with sulphuretted hydrogen, the stannic sulphide formed was filtered out, and the filtrate, after freeing it from sulphuretted hydrogen with a stream of air, once more saturated with hydrochloric acid gas, which threw down the substance in an essentially pure state and nearly white. In all this work care must be taken to avoid heating the solutions, as the chloride of pentamidobenzol, after the reducing agents have been removed, is easily decomposed by heat into a black tar; the solutions, therefore, should never be concentrated by evaporation on the water-bath. We obtained a less pure substance also, if the solution in water and precipitation with hydrochloric acid gas was repeated more than once. The crystals were dried at first in a desiccator over calcic oxide, calcic chloride, and potassic hydrate, and finally heated to 70°–80° for about five hours in an air-bath. On analysis they gave the following results:

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[1] Barr succeeded in removing all the tin from his preparation in this way.

I. 0.2372 gram of the substance gave on combustion 0.2445 gram of carbonic dioxide and 0.1157 gram of water.

II. 0.1827 gram of the substance gave 0.1880 gram of carbonic dioxide and 0.0880 gram of water.

III. 0.1533 gram of the substance gave 35.8 cc. of nitrogen at a temperature of 14.2° and a pressure of 750 mm.

IV. 0.1457 gram of the substance gave according to the method of Carius 0.2377 gram of argentic chloride.

	Calculated for $C_6H(NH_2)_2(NH_3Cl)_3$.	Found.			
		I.	II.	III.	IV.
Carbon	27.43	28.11	28.06	...	...
Hydrogen	5.33	5.42	5.35	...	...
Nitrogen	26.67	...	...	27.08	...
Chlorine	40.58	...	...	...	40.33

Considering the ease with which the substance is decomposed, the agreement between these results and those calculated from the formula is as close as can be expected. The method of purification described above, however, does not always give such satisfactory results. Samples from two other preparations gave numbers which differed by about one per cent. from those corresponding to the formula, the chlorine being too low and the other constituents too high by this amount; but we ascribe this to partial decomposition of the substance during the purification, as both of these specimens were much darker in color than that which gave the more satisfactory analyses. The objection which might be founded on these results, that our substance was not a definite compound, but a mixture of ammonic chloride with some organic body less rich in nitrogen than the chloride of pentamidobenzol, is removed by the microscopic examination of the substance, which showed that it consisted of well-developed rhombic crystals without any admixture whatever, to which may be added the fact that chlorplatinic acid gave no precipitate with a solution of the substance.

Properties.—The trichloride of pentamidobenzol, as precipitated by hydrochloric acid from its aqueous solution, is seen under the microscope to consist of rather thick well-developed transparent rhombic plates, with the sharper angles truncated by a single plane. It is colorless when first prepared, but soon turns pink or gray, and on long standing passes through dark brown to black, a change which is much accelerated by heat; yet even after it has become nearly black, if examined with the microscope, it is found to retain unaltered its crystalline form, and the individual crystals are still transparent, although very much darkened, so that this change in color seems to have taken place only superficially. It is very easily soluble in water, but only slightly soluble in strong hydrochloric acid, a property which is useful in the purification of the substance. The aqueous solution decomposes quickly when heated, a black tar being formed, and a similar change takes place more slowly at ordinary temperatures, the solution becoming at first clear pink, and then darkening through shades of red to black. The action of more violent oxidising agents is described below, and resembles that of the air. The salt, when dry or moistened with strong hydrochloric acid, is much more stable than a solution, or the wet salt. The substance is sparingly soluble in alcohol and essentially insoluble in ether, benzol, or chloroform.

If ammonic hydrate is added with caution to a concentrated solution of the salt, a black jelly is precipitated; if the solution is dilute, no precipitate is formed, but the liquid takes on a pink color, which in a few minutes passes through purple and violet blue to a yellowish green; from this solution hydrochloric acid precipitates black flocks, which redissolve in an excess of the acid, or on the addition of ammonic hydrate. Sodic hydrate acts on the chloride in the same way. The free base seems to be insoluble in ether; at any rate, nothing was extracted by this solvent from an aqueous solution of the salt, to which an excess of sodic hydrate had been added. It is evident from the observations just described, that the isolation of the free base would be a matter of great difficulty.

The foregoing results correspond to those of Barr in every respect, except the crystalline form of the chloride, which he describes as white needles as fine as hairs. He also made the pentacetyl compound $C_6H(NHC_2H_3O)_5$.

Chlorplatinic acid with a solution of the trichloride of pentamidobenzol gives no precipitate at first, but after some time a slimy brown substance is deposited on the sides of the test-tube, evidently a product of oxidation. We are inclined to think, however, that the oxidising agent is the oxygen of the air rather than the chlorplatinic acid, as a similar result was obtained by the action of picric acid. Benzaldehyd added to a solution of the salt also gave a tarry product.

When the trichloride of pentamidobenzol is treated with nitric acid and ferric chloride, a deep purple solution[1] is formed, looking very much like potassic permanganate; and when an excess of the ferric chloride has been added, a brown flocculent precipitate is deposited, which when dried forms a hard mass of a brown color without crystalline form, since under the microscope it appears to be made up of sandy granules. It is slightly soluble in water, imparting to it a dark brown color. Preliminary analyses gave the following results:

0.1600 gram of the substance on combustion gave 0.2592 gram of carbonic dioxide and 0.0650 gram of water.

0.1685 gram of the substance gave according to the method of Carius 0.0797 gram of argentic chloride.

	Found.
Carbon	44.18
Hydrogen	4.51
Chlorine	11.69

We were engaged on the study of this substance when we received Barr's paper, and accordingly stopped our work on this subject, and we publish these analyses only because they may be of use to any one who may continue the investigation of this substance, as it would be idle to try to derive a formula from them until they have been supported by further work. Barr also observed the formation of this substance, but did not attempt to study it carefully, or analyse it.

It seems probable that the pentamidobenzol, in addition to the trichloride, can form a *pentachloride*, as one of our first preparations, in which the reduction was carried on at a lower temperature than usual, yielded a substance which, dried at first in a desiccator over calcic chloride without any alkaline absorbent, and finally for a short time in an air-bath at 90°, gave the following result on analysis:

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[1] Compare this with the action of air on a solution of the salt or of the free base described earlier in this paper.

0.1738 gram of the substance gave 30.9 cc. of nitrogen at a temperature of 6° and a pressure of 750 mm.

	Calculated for $C_6H(NH_3Cl)_6$.	Found.
Nitrogen	20.86	21.37

The appearance of Barr's paper has prevented us from making another attempt to prepare this substance. If it is a definite compound, it is a very unstable one, as it gave off a distinct smell of hydrochloric acid.

Trianilidodinitrobenzol, $C_6H(C_6H_5NH)_3(NO_2)_2$.

This substance can be made by heating for a short time aniline with tribromdinitrobenzol in the proportion of six molecules of the base to one of the bromine compound. It seems that the two substances do not act on each other in the cold, or, if there is any action, it is a very slow one, and in this respect the dinitro compound differs from the tribromtrinitrobenzol, which acts on aniline quickly at ordinary temperatures. The product was purified by crystallising it from alcohol till it showed the melting point 179°, dried at 100°, and analysed with the following results:

I. 0.1820 gram of the substance gave on combustion 0.4347 gram of carbonic dioxide and 0.0760 gram of water.

II. 0.1906 gram of the substance gave 26 cc. of nitrogen at a temperature of 12° and a pressure of 762 mm.

III. 0.1815 gram of the substance gave 26 cc. of nitrogen at a temperature of 17° and a pressure of 743 mm.

	Calculated for	Found..		
	$C_6H(NHC_6H_6)_3(NO_2)_2$.	I.	II.	III.
Carbon	65.31	65.13	...	...
Hydrogen	4.30	4.64	...	...
Nitrogen	15.88	...	16.24	16.24

Properties.—The trianilidodinitrobenzol, when crystallised from alcohol, forms vivid orange-red needles, which under the microscope appear as long prisms terminated by a single plane at angles not very far from right angles to the sides; occasionally groups of radiating needles are observed also. When crystallised from ether, it forms irregularly spherical crowded groups of short stout radiating prisms with blunt ends made up of several planes, a form which is decidedly characteristic. It melts at 179°, and is essentially insoluble in either cold or boiling water, or in ligroine;

slightly soluble in cold alcohol, freely in hot; moderately soluble in ether, carbonic disulphide, glacial acetic acid, or acetone; freely soluble in benzol or chloroform, but the substance is deposited from the two solvents last mentioned in an amorphous form, so that hot alcohol is the best solvent for it. Strong hydrochloric acid, either hot or cold, has no perceptible action on it. Strong nitric acid dissolves a very little, with a pale yellow color; strong sulphuric acid dissolves rather more of the substance, with a stronger yellow color. Upon heating it with either of these last two acids it is charred. It is therefore, as was to be expected, less basic in its properties than the triamidodinitrobenzol.

THE INDIAN GRASS OILS.

[*Preliminary Notice.*]

By Frank D. Dodge.

There are found in commerce at least five volatile oils, which appear to be obtained from various tropical grasses of the genus *Andropogon*. These are: oils of citronella, lemon-grass, Indian or Turkish geranium, ginger-grass, and vetivert or cus-cus. Much uncertainty has arisen in the effort to assign to each oil its proper botanical source, and in the identification of nearly related plants which afford commercially distinct oils.

The citronella plant appears to be the one known to botanists as *Andropogon nardus*, Linn., and is figured and fully described in Bentley and Trimen's "Medicinal Plants." This grass is quite common in the plains of the Punjab and the North-west Provinces, and is extensively cultivated in Ceylon, Singapore, and the Malabar coast. Some interesting details of the occurrence, uses, etc., of the grass and the manufacture of the oil are given in Watt's "Dictionary of the Economic Products of India" (1888).

As to the origin of "lemon-grass oil" there appears to be considerable doubt. The majority of botanical writers ascribe it to *A. schoenanthus*, Linn., while the best Indian authorities state that it is obtained from a different plant, which more closely resembles *A. nardus.* Hackel, in his Monograph of the Andropogoneae (1889), leaves the question undecided. The oil of lemon-grass is certainly distinct from all the others, and it seems probable that the grass is a peculiar species.

The important Turkish geranium oil, which also passes under the names of Rusa oil, Palmarosa oil, Nimar oil, and others, is probably derived from *A. schoenanthus*, Linn. It has been known and used for a long period. According to Pickering, the grass was employed as a perfume in the time of Alexander the Great. A description of the plant is given by Dr. Dymock ("Materia Medica of India"), and it is figured as *A. pachnodes* by Trinius (Sp. Gram. III, tab. 237). The grass is abundant in Central and Northern India; the preparation of the oil is described by Dymock, Watt, and others.

Ginger-grass oil appears to be a cheap and inferior variety of the geranium oil.

Oil of vetivert, or cus-cus, is obtained from the rhizome and root-fibres of *A. squarrosus*, Linn. (*A. muricatus*, Retz.). This grass was also known at an early date. It is very probably the sweet-scented "usira" root of the "birana" grass mentioned in the Dhammapada and other Sanskrit classics (Pickering). Vetivert grass occurs in many parts of India, and appears to be cultivated in Burmah. It is also found in Mauritius and the Philippine Islands, and is the only species of those under discussion which occurs in the New World, being abundant in the Antilles, Porto Rico, Jamaica, Brazil, etc. The oil of vetivert is manufactured in this country from grass imported from India, and finds an important application in perfumery.

Examination of Citronella Oil.

Gladstone in 1872,[1] by repeated distillation, separated the oil into two portions, one boiling at 202°–205°, the other at 199°–202°. On combustion, these gave figures from which he calculated the composition $C_{10}H_{16}O$. It is to be noted, however, that his results approximate more closely to the formula $C_{10}H_{18}O$.

In 1875, C. R. A. Wright[2] found the main constituent to be an unstable body of the composition $C_{10}H_{18}O$, which on treatment with dehydrating agents gave rise to a terpene or terpenes, but not cymene. The latter was obtained, however, by heating with bromine. He found that the oil was altered by repeated distillation, high-boiling resinous products being formed.

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[1] Jour. Chem. Soc. (2) **10**, 7.

[2] Jour. Chem. Soc. 1875, 1.

Flückiger, in his "Pharmacographia," made the important observation that both citronella and lemon-grass oils yield solid compounds when shaken up with bisulphite solution. This fact immediately suggested the method of investigation. It appears that Mr. Kremers also (of whose work the writer was unaware until after the results described below had been obtained) took advantage of this observation.

Kremers[1] treated the oil with strong bisulphite solution, filtered out the white precipitate, and washed with alcohol. The bisulphite compound was decomposed by dilute sulphuric acid at a gentle heat, and the sulphur dioxide removed by dry potassium carbonate. The aldehyde obtained thus was a viscid yellow liquid, possessing a geranium-like odor. Its specific gravity was 0.942. On fractionation it decomposed. Analyses gave figures approximating to the formula $C_7H_{14}O$, but the boiling point was not ascertained. From these data the aldehyde was concluded to be a heptoic aldehyde, isomeric if not identical with oenanthol. The oil filtered from the bisulphite compound was by fractionation separated into two portions: one, boiling below 200°, appeared to be an impure terpene, $C_{10}H_{16}$; the other, boiling between 217° and 222°, on analysis gave:

		Calculated $C_{10}H_{18}O$.
C	77.96	77.92
H	12.27	11.69

Kremers found this substance to be different from eucalyptol, and suggested that the name citronellol be retained for it. It is evident that Kremers' results differ greatly from those of Wright. The former is of the opinion that the oil examined by Wright was really a variety of geranium oil, *i. e.* true oil of *A. schoenanthus*, as stated by Wright. According to Watt, however, Dr. Wright's material was probably citronella, erroneously ascribed to *A. schoenanthus.*

Three samples of citronella oil have been examined by the writer. The first is an oil manufactured on the Winter Estate, near Galle, Ceylon. This commands a higher price than other varieties, and is considered the purest. The second is what is known as "native" oil, a cheap variety, whose quality is considered uncertain. The third is a "native" oil redistilled in this country.

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[1] Proc. Amer. Pharm. Assn. 1887.

It is well known in the trade that citronella oils are largely adulterated with kerosene. Large quantities of the latter are imported at Ceylon, and it is quite improbable that all is used for illumination. Detection of the adulteration, however, is not difficult. Samples two and three were found to contain about 18 per cent. of kerosene, while a careful examination of sample one convinced the writer of its freedom from such impurity. All subsequent work was accordingly done on sample one.

This oil is clear light greenish yellow, with a sharp burning taste and rather powerful aromatic odor. Its density at 16° is 0.8770; at 26.5°, 0.8750. This agrees fairly well with Gladstone's figures, 0.8741 and 0.8750 at 20°. Kremers, however, found the density of his material to be 0.8833. On distillation the oil passes over between 200° and 240°, leaving about 10 per cent. of thick oily residue, possessing a pungent odor. Continued fractioning did not yield good results, as the oil appeared to decompose on long heating.

When shaken with a saturated solution of sodium bisulphite, after ten minutes the liquid solidifies with considerable evolution of heat. On standing, the mass becomes yellow on the surface, owing to oxidation of other constituents of the oil. The bisulphite compound is readily obtained pure by thinning with ether or chloroform, filtering, and washing with the same solvents, in which the precipitate is practically insoluble. Alcohol does not work so well. The bisulphite precipitate is readily decomposed by acids, alkalies, sodium carbonate, or hot water, which regenerate the aldehyde. All fractions of the oil yield precipitates with bisulphite solution; the first fractions, however, the more readily.

Phenylhydrazine combines with the oil with evolution of heat. On testing the successive fractions, it was noticed that the first reacted more readily than the others, indicating that the aldehyde or aldehydes were among the more volatile constituents of the oil.

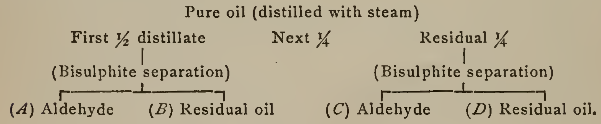
Ammoniacal silver solution, when mixed with the oil and allowed to stand, yields very readily a mirror, followed by a thick lustrous deposit of metal.

Acetyl and benzoyl chlorides react with great readiness, but no solid compounds could be detected among the products of the reaction. Ammonia under ordinary conditions appears to be without action on the oil.

Isolation of the Aldehyde.

The washed bisulphite compound, freed from ether by short exposure to the air, was gradually added to a warm solution of sodic carbonate and kept warm until all the white precipitate had disappeared. The supernatant oil was then separated and dried. On distillation, the greater part boiled from 200°–210°, leaving a thick residue, which did not react very readily with phenylhydrazine. This indicated an alteration of the aldehyde, due to the heat of distillation. To avoid this difficulty, the oil liberated from the bisulphite compound was immediately distilled in a current of steam. This plan succeeded admirably, a pure white oil passing over, and a small quantity of dark-colored oil remaining in the flask.

In order to ascertain whether possibly a mixture of aldehydes or ketones were present in the oil, a large amount was treated after the following plan:



Should the portions (*A*) and (*C*) differ, it would be fair to assume that there were two or more constituents having ketonic properties. If they were found to be identical, probably but one aldehyde was present in the oil.

2 liters of oil were treated in this way. For the preparation of the aldehyde, the first portion of the distillate (1100 cc.) was divided into four parts of about 280 cc. each. The bisulphite solution contained 1000 grams dry sodium bisulphite dissolved in 2 liters of water. 250 cc. of this was added to each portion of oil and the mixture well stirred. During the stirring the vessels were kept cool with ice water. After about ten minutes the mixture "set," forming a snow-white magma. The remainder of the bisulphite was now added gradually, stirring all the time. A further evolution of heat took place until all the oil had been precip-

itated. After standing about an hour the mass was wrapped in flannel, and after draining on a large funnel, was carefully pressed in a filter-press. When the mass was pretty dry it was removed from the press, thinned out thoroughly with ether, and again drained and pressed. The bisulphite compound was now tolerably free from residual oil. To remove the ether it was exposed to the air for several hours. At this stage it has the appearance of wax or soap; on long exposure it decomposes, turning yellow on the surface.

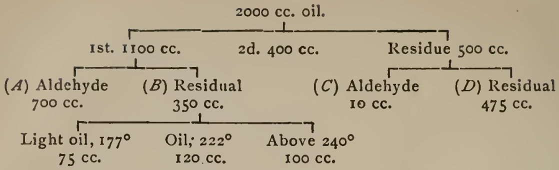
To liberate the aldehyde, the dry mass was mixed with crystallised sodic carbonate, 450 grams of the former to 350 grams of the latter, in a large flask. Steam was then passed into the mixture, which soon liquefied and yielded a distillate of, in this case, about 250 grams. The total yield of aldehyde (portion *A*) amounted to 700 cc.

The filtrate from the bisulphite precipitate was then worked up. The oil yielded by the first pressing was collected apart. The ethereal washings were dried and, after removal of the ether, combined with the first. The product, a light yellow oil of peculiar odor, amounted to about 350 cc.

This oil was now carefully fractionated. It commenced to boil at 185°, and the temperature rose steadily to 240°, above which it was considered unnecessary to fraction. At the tenth distillation the oil was almost completely separated into three portions. The first, a limpid colorless oil having a lemon-like odor, boiled at 177°–180°, and amounted to 75 cc. The second, a somewhat thicker oil, of slightly greenish color and having a pleasant rose-like odor, boiled at 222°–224°, and amounted to 120 cc. The third portion consisted of products boiling above 240°, and was a dark-brown viscid liquid having a pungent odor.

The residual 500 cc. of oil, not readily volatile with steam, was treated with bisulphite in the same manner as the first portion, but using much less bisulphite. After a few days the bulky precipitate was filtered out, pressed, washed, and the aldehyde liberated as before. About 10 cc. only were obtained, which resembled in appearance, odor, taste, and behavior on heating, the aldehyde obtained from the first distillate, and is almost certainly identical with it.

The results of the analysis may be concisely represented by the diagram:



The second distillate of 400 cc. was not further examined. The portion (*D*) was fractionated. It behaved like portion (*B*), but yielded a much larger amount of high-boiling products, which oxidise readily and are difficult to treat.

Properties of the Aldehyde.

The steam-distilled aldehyde, after drying several days over calcic chloride, is a colorless oil, of peculiar, not unpleasant odor and sharp acrid taste. The specific gravity at 25° was found to be 0.8509. It commences to boil at 202°, and the temperature slowly rises to 207°, after which it rises more rapidly, and a resinous mass remains in the flask.

On combustion:

I. 0.24725 gram oil gave 0.2723 gram H_2O and 0.7008 gram CO_2.

II. 0.2627 gram oil gave 0.2766 gram H_2O and 0.7483 gram CO_2.

III. 0.2064 gram oil gave 0.2193 gram H_2O and 0.5888 gram CO_2.

A sample of aldehyde was washed with dilute potassic hydrate to remove any acid possibly present from oxidation, and again dried. From this:

IV. 0.2184 gram oil gave 0.2369 gram H_2O and 0.6247 gram CO_2.

V. 0.2039 gram oil gave 0.2230 gram H_2O and 0.5825 gram CO_2.

	Calculated $C_{10}H_{18}O$.	I.	II.	III.	IV.	V.
C	77.92	77.29	77.68	77.80	78.00	77.91
H	11.69	12.23	11.69	11.80	12.05	12.14

The aldehyde is then isomeric with borneol and geraniol. The name *citronellic aldehyde* seems suitable as indicating its origin.

A vapor density determination by the method of Victor Meyer gave, $D = 5.405$: calc. $= 5.34$.

Citronellic aldehyde appears to be dextro-rotary: a column 2 decimeters long produces a deviation of about 7° for sodium light. Exact measurements are in progress.

The aldehyde readily absorbs bromine, the solution becoming warm. If the temperature rises too much, hydrobromic acid is given off and decomposition takes place. To determine the amount of bromine absorbed it was found convenient to weigh quickly about 1 gram of aldehyde, dissolve it in 20 cc. of chloroform or carbon disulphide, and run in, from a burette, a standardised solution of bromine in carbon disulphide, until a slight permanent red coloration was obtained. The bromine solution used contained 0.1163 gram bromine per cc. The following results were obtained:

I. 1.084 gram aldehyde required 9.0 cc. Br solution.
II. 1.885 gram aldehyde required 16.2 cc. Br solution.
III. 2.0149 grams aldehyde required 17.5 cc. Br solution.

Per cent. Br in bromo-derivative:

I.	II.	III.	Calculated Br_2.	Br_4.
49.1	49.9	50.3	50.9	67.5

These results, though only approximate, yet are sufficient to show that the unsaturation of the aldehyde is equivalent to two atoms of bromine.

Action of Heat on the Dibromide.

112 cc. of the bromine solution used above was gradually added to 12 grams of the aldehyde. The carbon disulphide was removed on a water-bath, and the residual liquid gradually heated to 120°, when torrents of hydrobromic acid were evolved. When this ceased, the residue was made alkaline and distilled with steam. The oil passing over was collected in ether, dried, and the ether driven off on a water-bath. A yellow oil amounting to 2 cc. was obtained, which possessed the odor of cymene, and on oxidation with hot permanganate solution yielded an insoluble acid, apparently terephthalic acid. This confirms Wright's statement; the reaction, however, is by no means quantitative.

Reduction of the Aldehyde.

25 grams aldehyde were mixed with 13 grams glacial acetic acid. 400 grams of 5 per cent. sodium amalgam were gradually added,

with occasional washing to remove the acetate formed. The resulting liquid was dissolved in ether, shaken up with bisulphite solution to remove any unchanged aldehyde, boiled with a little alkali to saponify any acetic ester possibly formed, washed, dried and distilled. The greater part boiled at 225°–230°. It gave no reaction with phenylhydrazine. It decolorised bromine solution, and possessed a pleasant odor of roses.

On combustion:

0.1972 gram oil gave 0.5550 gram CO_2 and 0.2299 gram H_2O.

	Calc. $C_{10}H_{20}O$.	Found.
C	76.92	76.75
H	12.82	12.95

This, then, is evidently the alcohol corresponding to citronellic aldehyde. On heating with acetic anhydride it yields a (probably) acetyl derivative, which has a curious quite characteristic odor.

Condensation Products.

Phenylhydrazine combines with the aldehyde very readily: on mixing the two liquids in equivalent proportions a turbidity soon appears, and a vigorous evolution of heat takes place. On chilling the resulting liquid, crystals soon form, and a semi-solid mass is obtained. The compound does not appear to be stable, however, as all attempts to isolate it in a crystalline condition were fruitless.

Aniline behaves similarly: the liquid product possesses a strong and rather disagreeable odor. Para-toluidine yields a similar compound. Attempts to prepare a condensation product with benzoic aldehyde were without result.

Acetyl chloride reacts vigorously with the aldehyde: the products have not yet been examined.

The acid corresponding to the aldehyde has not yet been obtained pure. Ordinary oxidising agents appear to split up the molecule, yielding fatty acids, etc. Potassium permanganate yields a mixture of acids, which smells strongly of ordinary valerianic acid.

Action of Phosphoric Anhydride on the Aldehyde.

Phosphoric anhydride acts very energetically upon citronellic aldehyde, and, unless kept cool, the liquid soon boils, and forms gummy products.

50 grams aldehyde were placed in a flask cooled by ice.

Phosphoric anhydride was added in small portions, with constant agitation, until no further heating occurred. The oxide was converted into a reddish curdy mass, and the liquid assumed a yellow tint. 200 cc. water and 100 cc. ether were now added, the mixture shaken well, and allowed to stand 24 hours. The liquid was then filtered from a white crystalline sediment, the yellow viscid ethereal solution separated from the watery layer, the latter again extracted with ether, and the combined ethereal solutions dried over calcium chloride. The ether was now removed on a water-bath and the residual oil fractioned. Between 140° and 180° a light oil passed over with some water. The temperature then rose rapidly to above 300°, when a thick oil passed over, which possessed a pleasant odor resembling the high-boiling fractions of citronella oil.

The light oil, after drying, was found to boil quite constantly at 175°–178°. It was heated with sodium for an hour on the water-bath, which produced a small brown precipitate.

On redistillation it boiled at 175°, and on combustion:

I. 0.1912 gram oil gave 0.2090 gram H_2O and 0.6125 gram CO_2.

II. 0.2343 gram oil gave 0.2556 gram H_2O and 0.7500 gram CO_2.

	Calc. $C_{10}H_{14}$.	$C_{10}H_{16}$.	Found. I.	Found. II.
C	89.55	88.23	87.36	87.29
H	10.44	11.76	12.14	12.13

This, then, is an impure terpene. To which class of terpenes it belongs has not yet been determined.

The white crystalline precipitate, filtered from the liquid containing the products of the action of phosphorus pentoxide, was washed with ether and dissolved in a little ether-alcohol, and allowed to crystallise. In 24 hours, large square colorless plates were deposited, which melt above 140°. The yield was about 2 grams. Another preparation furnished beautiful transparent prisms. They contain phosphorus, but have not yet been carefully examined.

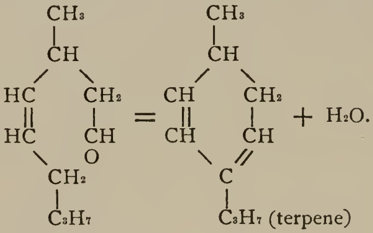
Constitution of Citronellic Aldehyde.

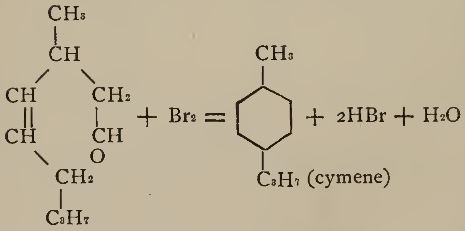
Although it may be a little premature to discuss the structure of this aldehyde, without more definite results, still the following considerations are of interest. By reason of its unsaturation the aldehyde cannot possess a "closed-chain" nucleus; moreover, none of its derivatives, except the phosphoric compound mentioned, have been induced to crystallise, while the closely related borneol and menthol series, which possess "ring" nuclei, crystallise readily.

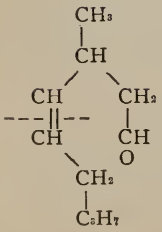
The easy conversion into a terpene and into cymene, and the very probable occurrence of valerianic acid among the oxidation products, are of great importance in fixing its structure.

The formula which most satisfactorily explains the chemical properties of the aldehyde is that of β-methyl δ-iso-butyl allyl-acetic aldehyde:

$$C_4H_9—CH=CH—CH(CH_3)—CH_2—COH:$$







On oxidation it should give valerianic and pyrotartaric acids, the latter of which would readily lose carbon dioxide and pass into butyric acid. The asymmetry of the β-carbon atom may account for its optical activity.

Much work, however, remains to be done before any formula can be assigned with certainty to the aldehyde.

Examination of the Constituent of b. p. 177°.

This oil is a light limpid liquid, having a very pleasant citrine odor. On combustion:

I. 0.2397 gram oil gave 0.2502 H_2O and 0.7444 gram CO_2.
II. 0.2695 gram oil gave 0.2854 H_2O and 0.8362 gram CO_2.

	Calc. $C_{10}H_{16}$.	I.	II.
C	88.23	84.8	84.6
H	11.76	11.6	11.7

The oil was evidently impure, and was distilled over sodium, which caused the separation of a dark flocculent precipitate. On combustion:

I. 0.1704 gram oil gave 0.1840 gram H_2O and 0.5377 gram CO_2.
II. 0.2049 gram oil gave 0.2176 gram H_2O and 0.6459 gram CO_2.

	Calc. $C_{10}H_{16}$.	I.	II.
C	88.23	86.05	85.90
H	11.76	11.9	11.7

These results are a little better, but it is evident that the oil retains a little of an oxygen compound very tenaciously. A vapor density determination by Meyer's method gave $D = 4.96$; calc. $= 4.70$.

The quantity of substance at my disposal was not sufficient to permit further treatment, and it was not possible to determine whether this terpene was identical with limonene, with which it agrees in boiling point. An attempt to prepare a solid tetrabromide was unsuccessful.

Examination of the Constituent of b. p. 222°.

This oil is a somewhat syrupy liquid, resembling in odor the citronellyl alcohol obtained by reduction of the aldehyde. On combustion:

0.2342 gram oil gave 0.2563 gram H_2O and 0.6693 gram CO_2.

	Calc. $C_{10}H_{18}O$.	$C_{10}H_{20}O$.	Found.
C	77.92	76.92	77.8
H	11.70	12.82	12.15

Its specific gravity at 26.5° was found to be 0.8741. This substance appears to have the properties of an alcohol. Acetic anhydride converts it into a product possessing the characteristic odor of the acetyl derivative of citronellyl alcohol. With sodium, evolution of hydrogen occurs slowly in the cold, more rapidly on heating. The sodium compound is insoluble in ether, and when treated with acetyl chloride affords the same derivative as that obtained by direct action of acetic anhydride. These facts led me to doubt whether the composition $C_{10}H_{18}O$ could truthfully be assigned to this compound. In fact, remembering the tenacity with which the terpene retains traces of this oxygen compound, it seemed more than probable that the latter was equally contaminated with terpene, the result of which would be to raise the percentage of carbon.

Further, the occurrence of an aldehyde with an *isomeric* alcohol in an essential oil is quite anomalous, while numerous instances are known of aldehydes being accompanied by their *corresponding* alcohols.

To ascertain whether this was so, an attempt was made to purify the alcohol by means of the sodium compound. Sodium in small pieces was added to 10 grams of the supposed alcohol diluted with benzene, until no further evolution of hydrogen occurred on the water-bath. The pasty mass was then thoroughly pressed between filter papers and washed with ether. When dry it was suspended in water, decomposed by dilute hydrochloric acid, the separated oil collected in ether, and the ether solution dried and fractioned. An oil was obtained, boiling at 224°–226°. On combustion:

I. 0.2051 gram oil gave 0.2325 gram H_2O and 0.5648 gram CO_2.
II. 0.2378 gram oil gave 0.2610 gram H_2O and 0.6537 gram CO_2.

	Calc. $C_{10}H_{20}O$.	I.	II.
C	76.92	75.10	74.98
H	12.82	12.58	12.18

These results are far from satisfactory, yet it seems probable that the alcohol constituent of the oil is citronellyl alcohol, $C_{10}H_{20}O$.

The oil of tansy, examined by Bruylants,[1] bears a curious relation to oil of citronella. It was found to contain an aldehyde, $C_{10}H_{16}O$, the corresponding alcohol, $C_{10}H_{18}O$, and a terpene.

Examination of Other Grass Oils.

As far as I am aware, no extensive work has been published on oil of lemon-grass. Gladstone noted that it resembled citronella very closely; Flückiger has observed its behavior with bisulphite solution. With the latter it reacts exactly like citronella; the aldehyde obtained appears to be quite different from citronellic aldehyde, and is now under investigation.

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[1] Ber. d. chem. Gesell. 11, 449.

Oil of Turkish geranium has been carefully examined by Jacobsen,[1] who found it to contain a monatomic alcohol, geraniol, $C_{10}H_{18}O$.

Oil of ginger-grass has not yet been investigated. Oil of vetivert, by reason of its costliness, is somewhat difficult to work on. It appears to be quite different from all the other grass oils.

The study of these oils will be continued.

ORGANIC LABORATORY, SCHOOL OF MINES, N. Y., *Oct.* 1889.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture.

XIII.—THE MOLECULAR WEIGHTS OF CERTAIN SUBSTANCES AS INDICATED BY THE BOILING POINTS OF THEIR SOLUTIONS.

BY H. W. WILEY.

The apparatus with which the experiments to be described below were made, was devised in August of this year, and the experiments were commenced about the first of September. It was not my intention to publish the results of this work until they had been greatly extended, but the notice of the observations of Ernest Beckmann of his employment of the same method induces me to submit the data already obtained for publication.

I have no desire whatever to question Mr. Beckmann's priority in the use of the method, but it may be of interest to know that it was independently adopted by me, and all the data submitted below obtained before a notice of his work reached me in the *Chemisches Central-Blatt*, No. 7, 1889, this day received.

The apparatus employed consisted of an oval round-bottom flask, of about 200 cc. capacity, the neck of which was supplied with a side tube for the purpose of connecting it with an appropriate condenser. By this means the volume of the liquid employed was kept constant. The thermometer employed was accurately graduated to tenths, the distance between each tenth of a degree being so great that with the aid of the cathetometer used in reading it we could easily distinguish the .02 of a degree. The bulb of the thermometer was made to occupy the central portion of the liquid, the volume of which in all cases was 150 cc. To protect the bulb of the thermometer against the influence of the steam bubbles, it was covered with a double coating of fine copper foil. This method of coating the bulb of the thermometer of course precluded its use with substances easily reduced, such as silver and mercury salts.

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[1] Ann. Chem. (Liebig), **157**, 232.

Sodium chloride was the substance chosen to determine the factor for use. Carefully repeated determinations with this substance gave the following data: Substance taken, sodium chloride; volume of water, 150 cc.; weight of substance taken, 4.5 grams; weight of substance taken to 100 cc. of water, 3.0 grams; boiling point of water, 99.47°; boiling point of sodium chloride in solution, 99.93°; total rise of temperature, 0.46°; rise of temperature for 1 gram per hundred of substance, 0.1533°; molecular weight of sodium chloride, 58.5; factor $= 0.1533 \times 58.5 = 8.968$.

Using this factor as a constant, the following determinations have been made:

Substance taken.	Volume water.	Wt. substance taken in grams.	Wt. substance taken in grams to 100 cc. water.	Temperature of boiling water.
KCl	150	6.0	4.0	99.50
KBr	150	6.0	4.0	99.50
KI	150	9.0	6.0	99.50
KNO_3	150	6.0	4.0	99.50
$K_2Cr_2O_7$	150	18.0	12.0	99.50
$NaNO_3$	150	6.0	4.0	99.44
Sucrose	150	20.0	13.33	99.50
Oxalic acid	150	6.0	4.0	99.50

Substance taken.	Boiling temperature of solution of substance. C°.	Total rise of temperature. C°.	Calculated molecular weight.	Theoretical molecular weight.
KCl	99.85	.35	76.91	74.5
KBr	99.79	.29	123.7	119.0
KI	99.83	.33	163.1	166.0
KNO_3	99.83	.33	108.7	101.0
$K_2Cr_2O_7$	99.88	.38	283.2	295.0
$NaNO_3$	99.86	.42	85.4	85.0
Sucrose	99.70	.20	643.2	342.0
Oxalic acid	99.70	.20	179.4	90.0

In addition to the numbers given above, a large number of determinations have been made with substances containing water of crystallisation. In those cases the calculated molecular weight does not correspond either with the theoretical molecular weight, including the water of crystallisation, nor with the molecular weight of the anhydrous salt. These results seem to indicate that substances containing water of crystallisation exist in solution in a modified form, and the influence of this modification on the boiling point of the solution can only be determined by largely extended observations.

It is curious to note further, that in the two organic substances examined, the observed molecular weight obtained, using the same factor obtained by observations on the sodium chloride, is just about double the ordinary accepted molecular weight.

Since the factor for boiling solutions is so much less than that for the freezing mixtures, the determination of the molecular weight by the above method requires a solution considerably stronger than that used in Raoult's freezing method. The advantage, however, of having a mercurial column sensibly constant for long intervals of time renders it possible to make the observations with great accuracy.

To allow for the slight changes which take place in the boiling point of water under the conditions mentioned, I propose, hereafter, to use two pieces of apparatus, one of which shall contain water to be kept constantly in use, the observation of the boiling point of water and of the substance under examination being made at the same time. It is hardly necessary to mention that in such a case the thermometers employed would be carefully compared and the readings corrected accordingly. It is further necessary that the source of heat be sensibly constant, and we secure this by using a lamp with a certain sized flame, which remains unchanged throughout the whole series of observations.

For assistance in the analytical data obtained I am indebted to Mr. W. H. Krug.

WASHINGTON, D. C., *September* 14, 1889.

A RAPID METHOD FOR THE ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS.

By W. M. Burton.

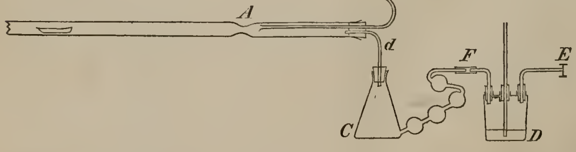
The method here described is a modification of that proposed by Sauer,[1] which consists in burning the substance in a stream of oxygen, absorbing the sulphur dioxide in bromine water containing hydrochloric acid, and determining the sulphuric acid as barium sulphate.

The indicator tropaeolin 00, however, not being sensitive to carbonic acid nor to alkaline sulphites, it is practicable to absorb the sulphur dioxide in an excess of a standard solution of potassium hydrate, and titrate back the excess of alkali by means of a standard acid, using tropaeolin as an indicator. In this way the titration can be made almost immediately after the combustion is completed, thereby avoiding the tedious operation of evaporating the bromine and precipitating and weighing the barium sulphate, as is necessary in Sauer's method.

The Reagents.

1. A dilute aqueous solution of tropaeolin 00.
2. A standard solution of sulphuric acid of such strength that one cubic centimeter of it is equivalent to five milligrams of sulphur. Each cubic centimeter of such a solution would contain .015312 gram H_2SO_4.
3. A solution of potassium hydrate approximately equivalent to the sulphuric acid.

The Apparatus.



The combustion tube is arranged in the manner recommended by Sauer; the absorption apparatus is, however, somewhat modified, as shown in the accompanying figure. *C* is a flask with absorption bulbs containing the standard alkaline solution. Since the column of liquid in the bulbs exerts a pressure in the combustion tube sufficient to blow out the red-hot glass at *A*, it is necessary to relieve this by other means. This is accomplished by the three-necked bottle *D*, which contains a shallow layer of water, and is connected with the bulbs at *F* and with an aspirator at *E*. The degree of exhaustion is regulated by the screw-cock *E*, and increased or diminished pressure is indicated by the height of the water in the safety tube. It is recommended to maintain a slightly diminished pressure in the apparatus during the process of combustion.

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[1] Ztschr. anal. Chem. 12, 32 and 178.

Mode of Procedure.

An amount of alkali equivalent to fifteen cubic centimeters of the standard acid is measured into the absorption bulbs; distilled water is added until an amount of liquid is present sufficient to fill the first three bulbs. Any excess of water should be avoided, in order to prevent the alkaline solution from being drawn over into the bottle *D*. The apparatus is then arranged as indicated in the figure, *A* is heated red hot, and the combustion is carried out in the manner recommended by Sauer. After the substance has been completely burned, the tube is swept out by means of a current of air or oxygen, and the apparatus is allowed to cool.

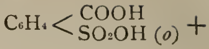
The combustion tube, the inlet tube for the oxygen, and the connecting tube *d* are rinsed with water to remove traces of sulphur dioxide or sulphur trioxide, and the rinsings are added to the liquid in the bulbs. A few drops of the tropaeolin solution are then added, and the excess of alkali titrated directly in the absorption bulbs. The change of the colored solution from yellow to red is quite sharp and distinct, allowing very close titration. The accuracy of the method was tested by determining the sulphur in samples of pure para-toluene-sulphamide, ortho-sulpho-benzoic acid and its acid ammonium salt. The results are given below.

Toluene-sulphamide(p).

Theoretical percentage of sulphur in $C_6H_4<\begin{matrix}CH_3\\SO_2NH_2\end{matrix}(p)$, 18.71.

Found: 18.90, 18.86, 18.65, 18.79, 18.80.

Ortho-sulpho-benzoic Acid.

Theoretical percentage of sulphur in  $C_6H_4 < \begin{matrix}COOH \\ SO_2OH\ (o)\end{matrix} + 4H_2O$, 11.68.

Found: 11.50, 11.60, 11.55, 11.62, 11.57.

Acid Ammonium Salt.

Theoretical percentage of sulphur in $C_6H_4 < \begin{matrix}COOH \\ SO_2ONH_4\ (o)\end{matrix}$, 14.61.

Found: 14.75, 14.81, 14.70, 14.68, 14.83.

The sulphur in a sample of crude petroleum was also determined by this method. As the percentage of sulphur in the oil was small, the standard solutions were diluted five times. The quantity of sulphur in the oil was also estimated by Carius' method. The results are given below:

By Carius' method: .53, .50, .48 per cent. S.

By method here described: .50, .49, .49 per cent. S.

It is, of course, evident that the sulphur in carbon compounds containing any of the halogens, phosphorus, or arsenic, could not be determined by this method, as there would be other acids formed which would vitiate the results.

CLEVELAND, *October*, 1889.

THE ACTION OF LIGHT ON SILVER CHLORIDE.[1]

BY ROMYN HITCHCOCK.

The plan of investigation, the first results of which I have the honor to bring before you at this time, was proposed by me in May, 1885. Since then I have mentioned the method several times in conversation, but it is only recently that I have been able to put it to a practical test.

The single set of experiments here described are only preliminary to a more thorough examination of the action of light, which, it is hoped, may be carried out in future. This includes a study of—

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[1] Read before the Chemical Section of the A. A. A. S., Toronto, 1889.

1. The action of light upon chemically pure haloids of silver.
2. The conditions which favor the decomposition of such compounds by light.
3. The products of the decomposition.
4. The activity of different parts of the spectrum in effecting the decomposition.

The subject is one which has been much studied, but we have scarcely more definite knowledge of the chemical effect of light upon the silver haloids now than was possessed in the time of Scheele, in 1777. I have been carefully over most of the literature of the subject, and it is quite extensive, but the results are confusing and contradictory. Even such an apparently simple question as whether there is a loss in weight when silver chloride is exposed to light, has only been satisfactorily settled by the recent work of Prof. Spencer Newberry. Yet the fact that chlorine is set free by the action of light was conclusively proved by Scheele, and that the quantity set free is not inconsiderable is evident from the strong odor observed.

I will not detain you by reviewing even the more important experiments recorded in the past, but will pass on to the considerations which led me to adopt a different method of experimenting. Recognising that there must either be a loss in weight corresponding to the weight of chlorine set free, or else that the chlorine must be replaced by some other element, it seemed quite plausible that an oxychloride might be formed by the action of light, as has been suggested by different writers. If two atoms of oxygen should take the place of one atom of chlorine in some unaccountable manner, then no appreciable change in weight would result. Seebeck and Abney have observed that silver chloride is not acted upon by light except in the presence of moisture, and Hodgkinson concluded that an oxychloride was formed, from which he obtained a small quantity of oxygen by heating it in an exhausted tube. This experiment, and those of Dr. W. Schmid[1] on the decomposition of plumbic iodide by light, seemed to lend strength to a rather improbable hypothesis.

Nevertheless, the subject seemed to deserve a more critical examination, and I determined as the first step not only to weigh the chloride before and after exposure to light, but also to determine the amount of chlorine set free. If an oxychloride is formed, the weight of chlorine set free must exceed the loss in weight of the chloride.

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[1] Pogg. Ann. 127, 7 (1866), 493.

But the discrepancies in the results of observations on the loss in weight were too great to be overlooked. Why, for example, should von Bibra find that there is no loss in weight, while Prof. Newberry found a very considerable change? I will answer this question as we go on. First, I wish to remind you of von Bibra's method of working. He filled small watch-glasses with white chloride and exposed them to sunlight under bell-jars for five weeks, the chloride being occasionally stirred to expose fresh surfaces. No loss in weight could be detected. The darkened product yielded no silver to nitric acid, but ammonia dissolved the greater part of it, leaving a residue soluble in nitric acid.

In thinking over the subject I became convinced that in all experiments up to this time the action of light upon the chloride has been only superficial. The energy required to effect the separation of the haloid must be considerable, for, as Draper showed long ago, even the thin film of a daguerreotype plate absorbed the active rays so effectually as to render a beam reflected from one sensitised surface inactive upon another. It therefore became necessary to obtain the chloride in a very finely divided condition, in order to ensure the complete action of the light upon it.

To accomplish this result a number of thin slips of glass, such as are used for cover-glasses in mounting microscopical specimens, were numbered with a diamond, cleaned by boiling in nitric acid, washed, and placed in a desiccator over sulphuric acid. These were accurately weighed, and I may here state that throughout these experiments two, and usually three independent weighings, on different days, were made for each operation. These slips were placed on strips of glass lying on the bottom of a crystallising jar. A very dilute solution of silver nitrate was then precipitated with chlorhydric acid in a beaker, and while the glass slips were held in place, this milky liquid was poured over them. The jar was set aside in a dark closet until the precipitate had deposited. The supernatant liquid was very slowly drawn off with a siphon, and distilled water run in by the same means. The deposited chloride is extremely light and the slightest current in the water will wash it from the glasses. The siphon must therefore have one end drawn out to a rather small point, so that it shall act very slowly. This washing by decantation must be repeated many times on successive days, in order to allow the salts in solution to diffuse thoroughly through the water, for it is not safe to draw off the water entirely, leaving the surfaces of the slips uncovered. Finally the water was drawn off as perfectly as possible, and the jar set aside until the remaining water had evaporated and the slips were quite dry. They were then picked out with forceps and placed in a desiccator, where they were allowed to remain several days or a week. They were then weighed. All these operations were done by artificial light. Slips thus prepared have a beautifully even, translucent coating of white silver chloride. Print can be read through them with ease. The slips measured about ¾-inch in width by 1½ inches in length.

The slips were placed in a glass tube, drawn off at one end to receive a rubber connection from a set of bulbed U-tubes containing a solution of silver nitrate. The other end was closed with a tubulated rubber cork and connected with a hydrogen apparatus. The hydrogen was passed through silver nitrate before it entered this tube. The tube was long enough to take four slips. When all was ready the apparatus was set out on the top of the National Museum in bright sunlight at 11.15 A. M., August 19th, and kept running until 4.30 P.M., when the slips were returned to the desiccator, and the tube and U-tubes washed out into a beaker. It should be stated that the U-tubes were shielded from the light during the experiment by a covering of black paper.

The silver chloride from the U-tubes was determined by collecting it in a porcelain crucible. After the slips had remained over night in the desiccator they were weighed, and the next day weighed again. The results are given in full in the following table I.

SUMMARY OF RESULTS.

I. *From Hydrogen Apparatus.*

No.	Wts. of Slips.	Slips + AgCl.	Wt. of AgCl.	Slips exposed.	Loss.
1	Not used.				
2	.49575	.51870	.02295	.51775	.00095
3	.45840	.47420[1]	.01580	...	...
4	.45563	.48350	.02787	.48225	.00125
5	.49955	.52405	.02450	.52285	.00120
6	.44163	.46575	.02412	.46460	.00115
7	.38590	Lost	...	...	...
8	.33080	.35370	.02290	...	...

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[1] This slip was not more than two-thirds covered, as it was displaced in the precipitating jar and slid partly under one of the other slips.

The amount of chlorine set free by the action of light was found to be somewhat less than the total loss in weight of the four slips used, but allowing for experimental errors, the discrepancy is not considerable. I am confident that a closer agreement will be observed in future experiments. The results were:

Weight of crucible + AgCl,	4.0143
" " "	3.9982
" " AgCl,	0.0161
Chlorine collected,	0.0040
Total loss in weight of slips,	0.0045

Prof. Newberry dissolved a quantity of silver nitrate corresponding to 0.1 gram of chloride in water and precipitated the chloride with sodium chloride. The precipitate was exposed to direct sunlight while a current of air was passed through the liquid. The precipitate was then weighed on a Gooch filter. From preliminary experiments he found that the precipitated chloride, before exposure to light, weighed .0996 to .0997 gram instead of 0.1000 gram. The metallic silver was weighed after dissolving out the chloride on the filter with ammonia. His results are thus given after exposure to sunlight:

	Weight.	Loss.	Met. Ag.	Met. Ag calc. from loss.
1	.0967	.0029	.0054	.0085
2	.0979	.0018	.0076	.0054
3	.0969	.0027	.0078	.0081
4	.0982	.0015	.0062	.0045

Placing the results of Prof. Newberry's experiments and of my own side by side, and reducing them both to represent the loss in weight of .1 gram of silver chloride, we have these figures:

		Loss.	
	Weight of AgCl.	Newberry.	Hitchcock.
1	0.1000 gram.	.003	.00418
2	0.1000	.0018	.00448
3	0.1000	.0027	.00490
4	0.1000	.0015	.00485

Two slips prepared as above, numbered 3 and 8 in table I, were exposed under a beaker-cover, without a current of gas or any attempt to collect the chlorine set free. The dry chloride taken from the desiccator was scarcely discolored in an hour in bright sunlight. A drop of distilled water on one of the slips caused immediate discoloration in the sunlight, confirming the idea that moisture is necessary for the reaction. The discoloration went on more slowly than in the hydrogen apparatus, and the exposure was continued for two days. The results show that in my experiments with the hydrogen apparatus the decomposition was not complete. The experiment should have continued over two days. It will be a matter of subsequent experiment to determine how long the action of light must continue to ensure its full effect.

The results of this last experiment are as follows:

No.	Glass.	Glass + AgCl.	Wt. of AgCl.	After Exp.	Loss.	Calc. for .1 gram.
3	.4584	.4742	.0158	.47325	.00095	.0060
8	.3308	.3537	.0229	.35230	.0014	.0062

It would appear that while the limit of the action of light may not have been reached even in the last experiments, the action proceeds regularly and is proportionate to the duration of the exposure, when the chloride is thus finely divided.

It will be obvious, from a consideration of the figures, that the results cannot be accepted as final, for it is doubtful whether the product representing the ultimate action of light has yet been obtained. It has not been deemed profitable to speculate upon the composition of such a product at this stage of the experiments.

I would state, however, that the product of the action of light in one experiment (slip No. 3) gave up a very considerable portion of silver when heated with dilute nitric acid. This fact, so directly opposed to all previous results, conclusively shows that the action of the light in these experiments has proceeded further among the particles than in those performed in the usual manner with the chloride in mass. The presumed protective action of a large excess of unchanged chloride upon the product of the reduction is to a great extent eliminated, and we find that product to be readily soluble. The bearing of this fact upon the sub-chloride hypothesis, and also upon the researches of M. C. Lea on his photo-salts of silver, is obvious.

Perhaps more may justly be claimed for the method than for the few preliminary results. I see no reason why the method should not lead to a solution of the problem of the action of light on the haloids of silver. We may thus accurately determine:

1. The loss of weight when light has fully acted on the compound.

2. The weight of the haloid set free by that action.

From these results one can readily determine whether or not the action is merely a setting free of the haloid, or the formation of a compound of silver with some other element, as oxygen for example, at the same time. The results already obtained clearly show, to my mind, that there is no such double decomposition, but they must yet be verified. Water seems to be necessary to the reaction, but it probably does not suffer decomposition.

In conclusion, I would express my indebtedness to Prof. F. W. Clarke, Chief Chemist of the Geological Survey, for affording me the laboratory facilities for carrying on this work, and also to Dr. Carl Barus for the use of the fine Bunge balance belonging to the physical laboratory of the Survey, on which all the weighings were made.

WASHINGTON, D. C., *August* 23, 1889.

REVIEWS AND REPORTS.

ON THE CONSTITUTION OF HYDROXYLAMINE AND ITS DERIVATIVES.

The discovery of hydroxylamine among the reduction products of nitric acid, by Professor W. Lossen,[1] in 1865, was not only of great theoretical interest, on account of the light which it threw upon the nature of this reduction, but it also enriched chemical science with a substance which was found to have most interesting and valuable properties. Hydroxylamine, as is well known, has become in recent years a most useful reagent for studying the structure of organic compounds. Its derivatives constitute several new and important classes of compounds. For example, the ease with which it reacts with substances containing the carbonyl group, $=CO$, has given rise to the formation of the compounds known as *oximes*, which are characterised by the group $=CNOH$. So also the nitriles, compounds containing the cyanogen group $-CN$, combine directly with hydroxylamine and form the so-called *amidoximes*, compounds which contain the group

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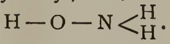
[1] Ann. Chem. (Liebig), Suppl. Bd. 6, 220.

$$-C{<}^{NH_2}_{NOH}.$$

On the other hand, owing to the readiness with which it can be decomposed and the nature of its decomposition products, hydroxylamine is used in inorganic chemistry as a powerful reducing agent. By means of it many metals, such as gold, silver, palladium, and mercury, can be precipitated in pure condition from solutions of their salts.

Ever since he discovered the compound Professor Lossen has carried on an investigation, the object of which has been to determine experimentally the structural formulas of hydroxylamine and its derivatives. As the compound is obtained by the reduction of nitric acid, and its composition is expressed by the formula NH_3O, the simplest conception of its constitution is to regard it as a substitution product of ammonia in which one hydrogen atom has been replaced by hydroxyl, thus,



$$H-O-N{<}^{H}_{H}.$$

Its formation from nitric acid would then be represented by the equation

$$H-O-NO_2+6H=H-O-NH_2+2H_2O.$$

This equation is analogous to that which represents the formation of amine bases from nitro compounds,

$$R-NO_2+6H=R-NH_2+2H_2O,$$

and, like the amines and ammonia, hydroxylamine unites directly with acids to form salts. These facts are in accordance with what would be expected of a compound having the structure represented above, but it is also evident that all the hydrogen atoms are not of equal value in this formula. Two of them are of equal value and bear the same relation to the nitrogen atom, but the third bears a different relation to the nitrogen; it is intimately associated with oxygen. From such a compound different substitution products should be obtained accordingly as the substituting group replaces the hydrogen of the hydroxyl group, or the hydrogen of the amido group. The plan of Lossen's work was to make substitution products of hydroxylamine, and by a comparison of their properties he hoped to get experimental evidence either for or against the formula.

In the first place he found[1] that substitution products of hydroxylamine can be prepared by the same methods that are used for making substitution products of ammonia. Thus when acid chlorides are treated with ammonia, acid amides are obtained, for example,

$$\underset{\text{Benzoyl chloride.}}{C_7H_5OCl}+2NH_3=\underset{\text{Benzamide.}}{C_7H_5ONH_2}+NH_4Cl.$$

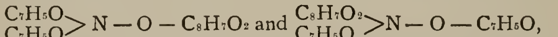
[1] Ann. Chem. (Liebig) **161**, 347.

In like manner acid chlorides and hydroxylamine give the so-called *hydroxamic acids.*

$$\underset{\text{Benzoyl chloride.}}{C_7H_5OCl} + 2NH_2OH = \underset{\text{Benzhydroxamic acid.}}{C_7H_5ONH_2O} + NH_3O.HCl.$$

Other hydroxamic acids were prepared by Lossen[1] in a similar manner, and the conclusion appeared justified that the hydroxamic acids bear the same relation to hydroxylamine that the acid amides bear to ammonia. By further treatment of the hydroxamic acids with acid chlorides a second and third acid group can be introduced into the compound. Thus benzhydroxamic acid on treatment with benzoyl chloride gives dibenzhydroxamic acid, and finally tribenzhydroxylamine. By simple reactions, as, for example, boiling with dilute hydrochloric acid, these substituting groups can be again eliminated from the compound.

In the early stages of the investigation[2] a large number of these hydroxamic acids were prepared and studied. It was soon observed that the disubstitution products exist in two isomeric conditions, and this fact is in accordance with the formula for hydroxylamine, there being two kinds of hydrogen atoms in the compound. But on examining the trisubstitution products, most remarkable and unexpected results were obtained;[3] thus tribenzhydroxylamine, made by replacing all of the hydrogen atoms with benzoyl groups, was obtained in three metameric forms, whereas theoretically but one such compound is possible. So also trisubstitution products containing two different groups were found to exist in more forms than are theoretically possible. Thus two dibenzanisylhydroxylamines are theoretically possible having the formulas



$$\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\!> N - O - C_8H_7O_2 \text{ and } \begin{matrix}C_8H_7O_2\\C_7H_5O\end{matrix}\!> N - O - C_7H_5O,$$

but it was found that three such compounds exist, each of which differs from the others in its properties.

A large number of other instances were noticed in which the number of isomeric compounds found was in excess of the number theoretically possible, and while in some cases it seemed probable that one and the same compound could exist in more than one physical modification, nevertheless the hypothesis of physical isomerism could not account for all the facts observed. Lossen finally reached the conclusion[4] that each of the three hydrogen atoms of hydroxylamine has a different value from the others, and further that each separate affinity of one and the same nitrogen atom may under certain circumstances act in a different manner from the others.

This conclusion rests primarily upon the assumption that the behavior of hydroxylamine and of ammonia towards acid chlorides is analogous, that substitution products of one are formed in the same way as are those of the other; that in the formation of benzhydroxamic acid, for example, the acid group benzoyl is present in the compound as a univalent group, thus $(C_7H_5O)H_2NO$, just as in benzamide the benzoyl group is in combination with the amido group $(C_7H_5O)NH_2$. This assumption appeared justified because the acid groups could again be eliminated unchanged from the molecule by the simplest reactions, and indeed no other method of explaining the action seemed possible at the time.

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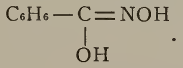
[1] Ann. Chem. (Liebig) **178**, 213.

[2] Ibid. **175**, 282.

[3] Ibid. **178**, 225.

[4] Ibid. **186**, 1; **186**, 55.

A more accurate knowledge of the behavior of hydroxylamine and the nature of its derivatives resulted from the study of the action of this substance upon aldehydes and ketones. Victor Meyer[1] and his co-workers carried out a series of important investigations upon the aldoximes and ketoximes, and came to the conclusion that the mode of action of hydroxylamine and ammonia is totally different. It was found that while ammonia in forming amido compounds must be present in the free condition and in concentrated solution; hydroxylamine, on the other hand, formed derivatives when present in extremely dilute solution and even when present as a salt. These and other investigations, especially those of Wallach, and Pinner upon the amidines, led Lossen finally to the view[2] that when acid chlorides and esters act upon hydroxylamine, the action takes place differently from that which obtains in the case of acid chlorides and esters acting upon ammonia. That benzhydroxamic acid, for example, instead of being a mono-substitution product of hydroxylamine, $\begin{matrix}C_7H_5O\\H\end{matrix}\!\!>\!NOH$, must be considered as a benzenyl compound having the structure



$$\begin{matrix}C_6H_6-C=NOH\\ \quad\;\;|\\ \quad\;\;OH\end{matrix}\ .$$

If the latter formula is the correct one for benzhydroxamic acid, then the difficulty of accounting for the numerous isomeric hydroxylamine derivatives disappears to a great extent. On the other hand, the formation of the compound by the action of benzoyl chloride upon hydroxylamine cannot be so easily expressed. The more recent investigations of Lossen[3] have brought more and more evidence in favor of the latter formula, so that at the present time he regards it as the only tenable one.

This view is based upon the following reasons: If benzhydroxamic acid is a benzenyl compound having the constitution represented by the formula $C_6H_5-C\begin{matrix}\diagup NOH\\ \diagdown OH\end{matrix}$, then it ought to be possible to prepare it by simple reactions from benzenyl compounds; and if in addition to this it is possible to effect the reverse change, that is, transform benzhydroxamic acid into benzenyl derivatives, then the formula may be regarded as proved. Both of these changes have been effected. In the first place, ethyl benzhydroxamic acid, an easily prepared derivative of benzhydroxamic acid, has been made by starting with benzimido ether. Benzonitrile in uniting with alcohol forms benzimido ether, and the latter substance by the action of hydroxylamine is converted into ethyl benzhydroxamic acid according to the equation:

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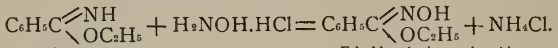
[1] Ber. d. deutsch. Ges. **15**, 2787. [2] Ibid. **16**, 873. [3] Ann. Chem. (Liebig) **252**, 170.



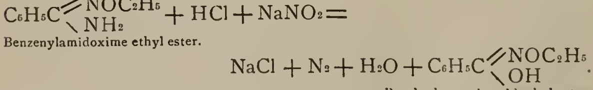
$$C_6H_5C\begin{array}{l}{=}NH\\ {-}OC_2H_5\end{array} + H_2NOH.HCl = C_6H_5C\begin{array}{l}{=}NOH\\ {-}OC_2H_5\end{array} + NH_4Cl.$$

Benzimido ether. Ethyl benzhydroxamic acid.

On heating the hydrochloric acid salt of ethyl benzhydroxamic acid, benzhydroxamic acid itself is obtained.

Secondly, the ethyl ester of benzhydroxamic acid has been prepared from benzenylamidoxime. The latter substance is formed by the action of hydroxylamine upon benzonitrile, and its structural formula as determined by Tiemann and Krüger[1] is $C_6H_5C\begin{array}{l}{=}NOH\\ {-}NH_2\end{array}$. By the action of ethyl iodide upon the sodium compound of this substance the ethyl ether is obtained, $C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}NH_2\end{array}$. If the hydrochloric acid salt of this ether be treated with nitrous acid, benzenylethoxime chloride is formed, a substance having the formula $C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}Cl\end{array}$. This chloride with sodium ethylate yields the ethyl ester of ethyl benzhydroxamic acid $C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}OC_2H_5\end{array}$, and the hydrochloric acid salt of the latter when heated gives the ethyl ester of benzhydroxamic acid.

Tiemann and Krüger,[2] who first studied the action of nitrous acid upon benzenylamidoxime ethyl ester, expected to get, as the immediate product of the action, benzhydroxamic acid ethyl ester according to the equation:



$$C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}NH_2\end{array} + HCl + NaNO_2 = NaCl + N_2 + H_2O + C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}OH\end{array}.$$

Benzenylamidoxime ethyl ester. Benzhydroxamic acid ethyl ester.

As they obtained the chloride $C_6H_5C\begin{array}{l}{=}NOC_2H_5\\ {-}Cl\end{array}$, and since this chloride cannot be formed by the direct action of hydrochloric acid upon benzhydroxamic acid ethyl ester, they conclude that the immediate product of the action, a compound which must have the constitution $C_6H_5C\begin{matrix}/\!\!/NOC_2H_6\\ \backslash OH\end{matrix}$, cannot be identical with benzhydroxamic acid ethyl ester, and therefore benzhydroxamic acid cannot have the formula $C_6H_5C\begin{matrix}/\!\!/NOH\\ \backslash OH\end{matrix}$. Lossen, however, in his last paper,[1] refutes this interpretation of the reaction, and maintains that the reaction takes place according to the equations:

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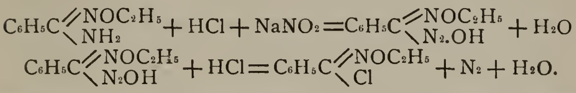
[1] Ber. d. deutsch. Ges. **17**, 1691.

[2] Ibid. **18**, 727.

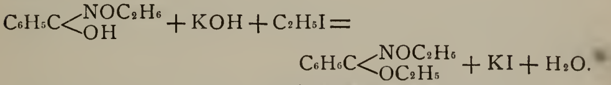


$$C_6H_5C\begin{matrix}/\!\!/NOC_2H_5\\ \backslash NH_2\end{matrix} + HCl + NaNO_2 = C_6H_5C\begin{matrix}/\!\!/NOC_2H_5\\ \backslash N_2.OH\end{matrix} + H_2O$$

$$C_6H_5C\begin{matrix}/\!\!/NOC_2H_5\\ \backslash N_2OH\end{matrix} + HCl = C_6H_5C\begin{matrix}/\!\!/NOC_2H_5\\ \backslash Cl\end{matrix} + N_2 + H_2O.$$

And as the chloride thus obtained can be converted into benzhydroxamic acid, it again proves that the latter is a benzenyl compound.

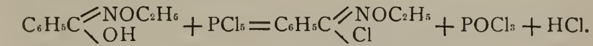
The reverse change, namely, the transformation of benzhydroxamic acid into benzenyl compounds, has been effected in several ways. The ethyl ester of benzhydroxamic acid by the action of ethyl iodide and caustic potash is converted into ethyl benzhydroxamic acid ethyl ester:



$$C_6H_5C < \begin{matrix}NOC_2H_6\\ OH\end{matrix} + KOH + C_2H_5I =$$
$$C_6H_6C < \begin{matrix}NOC_2H_6\\ OC_2H_5\end{matrix} + KI + H_2O.$$

Ethyl benzhydroxamic acid ethyl ester.

But the latter substance is a benzenyl compound which has been made by the action of sodium ethylate upon benzenylethoxime chloride. Further, the ethyl ester of benzhydroxamic acid can be directly converted into benzenylethoxime chloride by treatment with phosphorus pentachloride.

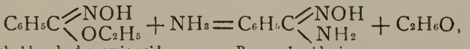


$$C_6H_5C\begin{matrix}/\!\!/NOC_2H_6\\ \backslash OH\end{matrix} + PCl_5 = C_6H_5C\begin{matrix}/\!\!/NOC_2H_5\\ \backslash Cl\end{matrix} + POCl_3 + HCl.$$

Benzhydroxamic acid ethyl ester. Benzenylethoxime chloride.

In a similar manner ethyl benzhydroxamic acid ethyl ester can be converted into the same chloride. But this chloride is undoubtedly a benzenyl compound, because it can be prepared by the action of nitrous acid upon benzenylamidoxime ethyl ester.

Ethyl benzhydroxamic acid has also been converted into benzenylamidoxime by the action of ammonia according to the equation:



$$C_6H_5C\begin{matrix}/\!\!/NOH\\ \backslash OC_2H_5\end{matrix} + NH_3 = C_6H_5C\begin{matrix}/\!\!/NOH\\ \backslash NH_2\end{matrix} + C_2H_6O,$$

Ethyl benzhydroxamic acid. Benzenylamidoxime.

and the ethyl ester of the acid, by similar treatment, gives the ethyl ester of benzenylamidoxime.

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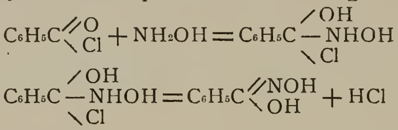
[1] Ann. Chem. (Liebig) 252, 181.

The results of the investigation may also be expressed in this way: The compounds benzhydroxamic acid, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NOH\\ \diagdown OH\end{smallmatrix}$, ethylbenzhydroxamic acid, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NOH\\ \diagdown OC_2H_5\end{smallmatrix}$, benzenylethoxime chloride, $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NOC_2H_5\\ \diagdown Cl\end{smallmatrix}$, and benzenylamidoxime, $C_6H_6\begin{smallmatrix}\diagup\!\!\diagup NOH\\ \diagdown NH_2\end{smallmatrix}$, can be readily transformed, by means of clean reactions, one into another, and the simplest explanation of their relationship is that they are all benzenyl compounds, as indicated by the formulas.

Benzhydroxamic acid being, therefore, a benzenyl compound, its formation from benzoyl chloride and hydroxylamine cannot be represented by the simple equation given above, but must be expressed by some such equations as the following:



$$C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{smallmatrix} + NH_2OH = C_6H_5C\begin{smallmatrix}\diagup OH\\ -NHOH\\ \diagdown Cl\end{smallmatrix}$$

$$C_6H_5C\begin{smallmatrix}\diagup OH\\ -NHOH\\ \diagdown Cl\end{smallmatrix} = C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NOH\\ \diagdown OH\end{smallmatrix} + HCl$$

according to which the hydroxylamine at first forms an addition product which immediately breaks up into hydroxamic acid and hydrochloric acid.

The constitution of benzhydroxamic acid having been determined, that of the other hydroxamic acid can be readily understood. Thus, by further action of benzoyl chloride, dibenzhydroxamic acid, a compound having the formula $C_6H_5C\begin{smallmatrix}\diagup\!\!\diagup NO(COC_6H_5)\\ \diagdown OH\end{smallmatrix}$ is obtained. And in a similar manner the constitution of the three isomeric dibenzanisylhydroxylamines is represented by the formulas:

$C_6H_5C(OCOC_7H_7O) = NO(COC_6H_5)$ dibenzanishydroxylamine,
$C_6H_5C(OCOC_6H_5) = NO(COC_7H_7O)$ benzanisbenzhydroxylamine,
$C_7H_7OC(OCOC_6H_5) = NO(COC_6H_5)$ anisdibenzhydroxylamine.

In this manner nearly all the cases of isomerism,[1] which in the earlier stages of the investigation seemed so inexplicable, can be accounted for, and no facts are at present known which indicate that the formula of hydroxylamine is different from that ordinarily assigned to it. The investigation is not yet finished, a number of the hydroxylamine derivatives exist in more than one physical modification, and a careful study is now to be made of the behavior and transformations of these substances. The phenomena of physical isomerism are receiving at present a great deal of attention from chemists, and Prof. Lossen thinks that it may be possible to explain the nature of these hydroxylamine derivatives by means of stereometric formulas.

E. H. KEISER.

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[1] Ann. Chem. (Liebig) 252, 195.

ON THE CONSTITUTION OF BENZENE.

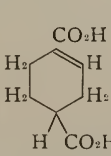
Since Kekulè's theory was proposed there has been, until recently, but little advance in our knowledge of the real constitution of benzene. The "ortho," "meta" and "para" positions have been established for groups in thousands of compounds, but these compounds can be equally well explained by the formula of Kekulè, of Claus, of Dewar, or of Ladenburg.

It would seem that the only means which can furnish a solution of the problem is a study of the transformation of members of the marsh gas series into benzene derivatives, or vice versa.

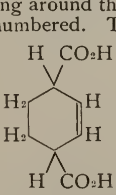
With this thought in mind, Baeyer[1] has shown that the quinone-hydro-dicarbonic ester obtained by Herrmann[2] from succinylo-succinnic ester is identical with the ester of dioxyterephthalic acid, and that it can be transformed into terephthalic acid. This furnishes a transformation of a hexamethylene derivative into a benzene derivative, and gives the first satisfactory refutation of Ladenburg's prism formula. A consideration of the prism formula shows that in the transformation into hexamethylene, only *one* of the three para positions can remain para, and the other two must become ortho. But in the transformation referred to, *two* pairs of groups in the para position remain para. This can be explained by Ladenburg's formula only by supposing such a wandering of groups from one position to another as is, to say the least, very improbable.

An extended study of succinylo-succinnic acid is difficult, owing to the ease with which it is decomposed. This led Baeyer[3] to take up, instead, the study of the reduction products of terephthalic acid.

To render more clear what follows, a few words must be said upon the nomenclature proposed for the hydro-terephthalic acids. The Greek letter Δ is used to represent a double union, and a numeral following it indicates the carbon atom from which the double union begins when passing around the ring in the direction in which the carbon atoms are numbered. Thus the two acids:



and



would be

Δ^1 tetrahydro-terephthalic acid,
and Δ^2 " " "

In the case of "geometric" isomers, to avoid the somewhat cumbersome terms fumaroid and maleïnoid, it is proposed to give compounds having groups on the same side of the plane of the ring the prefix "cis," while compounds having groups on opposite sides of the plane of the ring are called "cistrans." To indicate this kind of isomerism the Greek letter Γ is used. This nomenclature can be applied, also, to such compounds as fumaric and maleic acids, and, by use of the signs + and — (instead of cis, etc.), to the tartaric acids.

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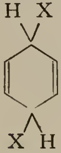
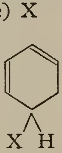
[1] Ber. d. chem. Ges. **19**, 428.
[2] Ann. Chem. (Liebig) **211**, 327.
[3] Ibid. **245**, 103, and **251**, 257.

A consideration of the structure of the hydro-terephthalic acids leads us to expect ten such acids. These have all been obtained by Baeyer, and the structure of each ascertained with a high degree of probability.

These acids are:

a. Dihydro-terephthalic acids.

1)


2)


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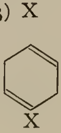

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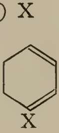

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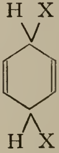
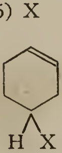


b. Tetrahydro-terephthalic acids.

6)


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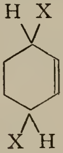

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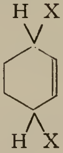
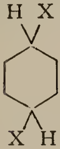
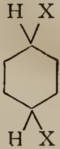


c. Hexahydro-terephthalic acids.

9)


10)


1) $\Delta^{2.5}\Gamma^{\text{cistrans}}$
2) $\Delta^{1.5}$
3) $\Delta^{1.4}$
4) $\Delta^{1.3}$
5) $\Delta^{2.5}\Gamma^{\text{cis}}$

6) Δ^{1}
7) $\Delta^{2}\Gamma^{\text{cistrans}}$
8) $\Delta^{2}\Gamma^{\text{cis}}$

9) Γ^{cistrans}
10) Γ^{cis}

The dihydro acids 1) and 5) are formed when terephthalic acid is reduced by sodium amalgam, the mixture being vigorously shaken and cooled, and carbon dioxide being passed through the solution to prevent the action of free alkali.

The proofs for the structure are:

1. Of the dihydro acids, only the $\Delta^{2.5}$ acid can exist in forms which are geometric isomers.

2. The acid takes up directly four atoms of bromine.

3. The acid contains two hydrogen atoms very loosely held in the molecule, the methyl ester losing hydrogen and being converted entirely into the ester of terephthalic acid merely by heating on the water-bath. The esters of the other dihydro acids do not conduct themselves in this way. Permanganate in alkaline solution oxidises the acid to terephthalic acid. This is not the case with the other acids. This is explained by the position of the two double unions which, by their negative nature, give to the hydrogen atoms the same mobility which we find in aceto-acetic ether and benzyl cyanide where a methylene group is situated between two negative groups.[1]

4. The acid is changed into the $\Delta^{1.5}$ acid by boiling the aqueous solution, and into the $\Delta^{1.4}$ acid by boiling with caustic soda. It has been shown in the case of hydro-muconic acid that such treatment causes a double union to shift from the $\beta\gamma$ to the $\alpha\beta$ position, and such a shifting can take place *twice* only with the $\Delta^{2.5}$ acid.

5. The acid is not further reduced by sodium amalgam in the cold, while each of the other acids is so reduced. It is found in other cases that a double union adjacent to the carboxyl group is much more easily reduced than a double union in the $\beta\gamma$ position.

The geometric isomers of the $\Delta^{2.5}$ acid are distinguished by their different solubilities, the Γ^{cistrans} acid being much more difficultly soluble than the other.

The $\Delta^{1.5}$ dihydro-terephthalic acid is obtained by boiling the $\Delta^{2.5}$ acid with water. This method of preparation, taken in connection with what has been said, gives one proof of the structure of the acid. A second proof is that sodium amalgam reduces the acid to the Δ^{2} tetrahydro acid. This is probably caused by the proximity of one double union to a carboxyl group, the latter by its negative character rendering the addition of hydrogen more easy.

The $\Delta^{1.4}$ dihydro acid is formed by the action of boiling caustic soda on either of the acids already described. The structure of the acid follows from the reasoning already given, the action of caustic soda being to cause the double unions to shift *toward* the carboxyl groups. This acid was erroneously called $\Delta^{1.5}$ in Baeyer's first paper. The reasoning against Kekulè's formula based on the conversion of the dibromide obtained from this acid into terephthalic acid lost its force when the true structure was established. This acid is the most stable of all the dihydro acids, and either of the other dihydro acids is converted into it by boiling with caustic soda. The $\Delta^{1.3}$ acid is, however, less easily transformed in this way than any other.

The $\Delta^{1.3}$ dihydro-terephthalic acid is obtained by boiling the $\alpha\alpha'$ dibrom-hexahydro-terephthalic acid (obtained from the hexahydro acid by direct substitution) with alcoholic potash. The proofs for the structure are:

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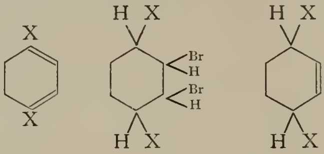
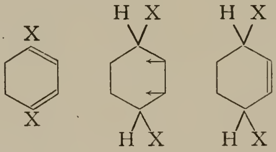
[1] Victor Meyer, Ber. d. chem. Ges. **20**, 534, 2944.

1. The $\Delta^{1.4}$ dihydro acid takes up two molecules of hydrobromic acid and gives a *para*-dibrom-hexahydro acid which is converted into hexahydro-terephthalic acid by the action of zinc dust and acetic acid. The $\Delta^{1.3}$ acid, on the other hand, gives with hydrobromic acid an *ortho*-dibrom-hexahydro acid which gives the Δ^2 tetrahydro acids when treated with zinc dust and acetic acid. The changes in the latter case are:



2. The dibromide of the Δ^2 tetrahydro acid gives the same $\Delta^{1.3}$ acid as the $\alpha\acute{\alpha}$-dibrom-hexahydro acid when treated with alcoholic potash.

3. Sodium amalgam reduces the $\Delta^{1.3}$ acid to the Δ^2 tetrahydro acids, thus:



An analogy for this case was wanting, but was furnished by Baeyer and Rupe,[1] who reduced dichlor-muconic acid, $CO_2H.CH = CCl - CCl = CH - CO_2H$, and obtained the $\beta\gamma$-hydro-muconic acid, $CO_2H.CH_2 - CH = CH - CH_2 - CO_2H$. This last acid cannot be further reduced till the double union shifts to the $\alpha\beta$ position. It seems that in the reduction hydrogen atoms are added directly to the two carbon atoms combined with carboxyl groups, and that the valences of the other two carbon atoms then unite, forming a double union in the $\beta\gamma$ (or Δ^2) position. The $\Delta^{1.3}$ acid may also be reduced to the Δ^2 tetrahydro acids by zinc dust and glacial acetic acid. This is the more remarkable as neither terephthalic acid nor any other of the hydro acids can be reduced in this way. This case shows very clearly the effect of the negative carboxyl groups in favoring the addition of hydrogen.

The $I'^{\text{cistrans}}\Delta^2$ and the $I'^{\text{cis}}\Delta^2$ tetrahydro-terephthalic acids are obtained by reducing the $\Delta^{1.3}$ dihydro acid with sodium amalgam or with zinc dust and glacial acetic acid; by reducing the $\Delta^{1.5}$ acid with sodium amalgam, and by reducing the 2.3 dibrom-hexahydro-terephthalic acid with zinc dust and glacial acetic acid. The structure follows from the methods of preparation, from the occurrence always of two "geometric" isomers, and from the fact that boiling with caustic soda converts both of the isomers into the Δ^1 tetrahydro acid. This is another instance of the shifting of the double union toward the carboxyl group under the influence of this reagent.

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[1] Ann. Chem. (Liebig) **251**, 278.

The Δ^1 tetrahydro-terephthalic acid is obtained by boiling the $\Delta^{1.4}$ dihydro acid, or terephthalic acid itself, with sodium amalgam, or by boiling the Δ^2 tetrahydro acid with caustic soda. The proofs for the structure are as follows:

1. The acid can have no *para* union between the carbon atoms, since it gives with hydrobromic acid a monobrom-hexahydro acid which is different from the α-monobrom-hexahydro acid obtained by direct substitution. The monobrom acid obtained from this acid must be a β compound, and, since both the α and β monobrom-hexahydro acid give the same tetrahydro acid by treatment with alcoholic potash, the double union must be in the $\alpha\beta$ position.

2. The acid takes up two atoms of bromine, and the dibrom-hexahydro acid obtained is identical with the dibrom acid obtained from the β-monobrom-hexahydro acid by direct substitution. When this dibrom acid is treated with zinc dust and glacial acetic acid, the tetrahydro acid is regenerated.

The Γ^{cis} and $\Gamma^{cistrans}$ hexahydro-terephthalic acids are formed by the reduction of the monobrom-hexahydro acids with zinc dust and glacial acetic acid. They are also formed by the reduction of any of the dibrom-hexahydro acids *which do not have the bromine atoms in the ortho position.* These acids conduct themselves in every respect as saturated compounds of the fatty acid series.

An interesting relation appears between the constitution of the acids and their solubility in water. A double union in the β position increases, while one in the α position decreases the solubility. A similar relation is also found for the melting points of the methyl esters.

The most important result of the investigation is, perhaps, the proof furnished that terephthalic acid does not contain three para unions, and, hence, that the Claus formula as ordinarily understood cannot be true.

The partially reduced acids contain double unions between atoms in the ortho position. They have the character of true unsaturated compounds. They take up bromine and hydrobromic acid directly, and they all reduce permanganate immediately. This last property Baeyer[1] has shown to be a very valuable means for distinguishing between saturated and unsaturated compounds. Terephthalic acid conducts itself in this respect as a saturated compound. Relying partly upon this and partly upon an erroneous structure for the $\Delta^{1.4}$ dihydro-terephthalic acid and the transformation of the dibrom addition product of that acid into terephthalic acid by alcoholic potash, Baeyer in his first paper drew the conclusion that Kekulè's formula cannot be true. He proposed in its place what he calls the "centric" formula, which he writes thus:

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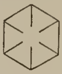
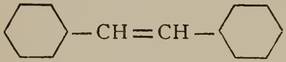
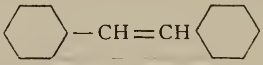
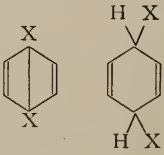
[1] Ann. Chem. (Liebig.) **245**, 146.



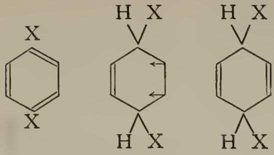
The idea which it is intended to express is that benzene contains a ring of six carbon atoms, and that one valence of each atom is directed toward the center of the ring. These valences mutually "paralyse" each other. They are held more firmly than is the case with double unions, since they are not attacked by permanganate, but less firmly than in the case of single unions, since terephthalic acid is reduced by sodium amalgam.

In his second paper, however, Baeyer says that while stilbene, , reduces permanganate instantly, phenanthrene, , does not. Whatever formula we assign to the two end benzene nuclei in phenanthrene the central nucleus must contain a double union. It seems, then, that this sort of a ring formation may give the double union the power to resist the action of permanganate and this objection to Kekulè's formula falls away.

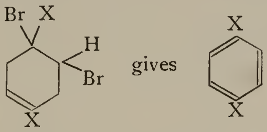
In his final discussion, Baeyer seems to leave the question entirely open between the "centric" formula, Kekulè's and Dewar's. Dewar's formula seems to explain, most easily, the formation of the $\Delta^{2.5}$ dihydro acid by direct reduction, thus:



In view of the conduct of dichlor-muconic acid, however, Kekulè's formula also explains satisfactorily the formation of this acid.



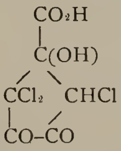
The transformation of the dibromide obtained from the $\Delta^{1.4}$ dihydro acid into terephthalic acid by alcoholic potash is explained most naturally by Kekulè's formula, thus:



Hantsch[1] has shown the formation of a collidin-dicarbonic ether from a dihydro compound containing the extra hydrogen atoms, one in combination with the nitrogen of the pyridine ring and the other in combination with the para carbon atom. This, perhaps, has a little weight in favor of Dewar's formula.

In the opinion of the author of this abstract, the lack of symmetry in Dewar's formula offers an objection very difficult to answer. It may be worthy of remark, also, that Dewar's formula ascribes to terephthalic acid two double unions in such a position as should render terephthalic acid easily soluble, while the position of the double unions in Kekulè's formula explains its difficult solubility.

Hantsch has recently obtained some interesting results by the action of sodium hypochlorite on the chloranilic and bromanilic acids and on phenol. The first product obtained from chloranilic[2] acid was a trichlor-diketo-pentamethylene-oxycarbonic acid having the formula



Under the influence of an oxidising agent this acid loses carbon dioxide and is converted into triketo-pentamethylene. This gives with phenyl-hydrazine a trihydrazone, which proves the presence of three carbonyl groups, and with bromine it gives trichlor-tribrom-acetone, $CCl_2Br.CO.CClBr_2$, and oxalic acid. The acid first obtained gives, also, an azine with toluylene-diamine, showing that it is an ortho-diketone. These reactions establish, conclusively, the formula which has been given. The transformations appear to take place as follows:

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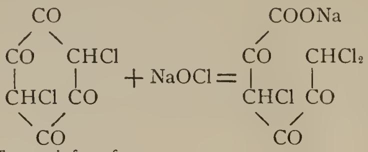
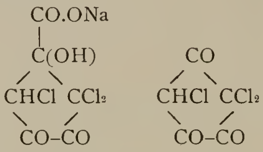
[1] Ber. d. chem. Ges. **18**, 2581.

[2] Ibid. **21**, 2432.

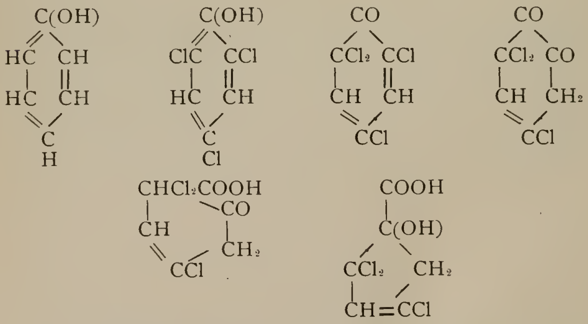


Tautomeric form of chloranilic acid.



Similar results were obtained with bromanilic acid.

Chlorine acting upon a solution of phenol in caustic soda[1] also produces a compound containing a ring of five carbon atoms, thus:



The limits of this paper forbid a detailed discussion of these formulae.

Zincke[2] has found that similar compounds can be obtained from *o*-amidophenol and from pyrocatechin, thus:

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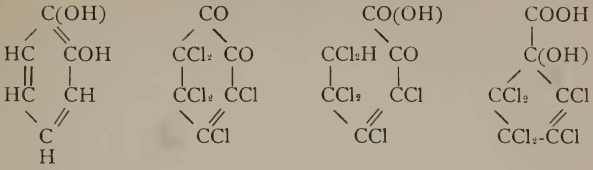
[1] Ber. d. chem. Ges. **20**, 2780; **22**, 1238.

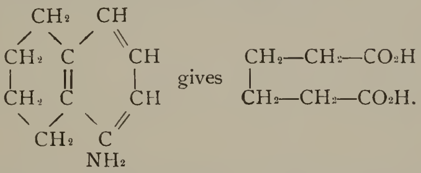
[2] Ibid. **21**, 2719, and **22**, 486.



From amido-β-naphthol and β-naphtho-quinone Zincke[1] has also obtained derivatives of indene and hydrindene in which one of the benzene rings of naphthalene has been transformed into a ring containing one less carbon atom.

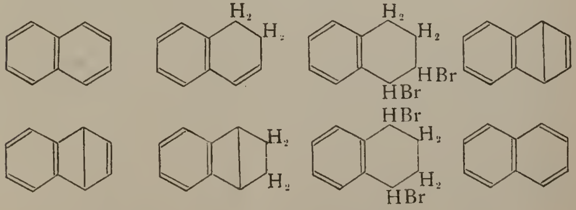
Nietzki and Benckiser[2] showed some time ago that croconic acid contains a ring of five carbon atoms, and that it can be formed from hexoxy-benzene.

Bamberger and Althouse[3] have obtained adipic acid by the oxidation of α-tetrahydro-naphthalene, thus:



In this case a normal chain of six carbon atoms is obtained. This furnishes a very satisfactory proof that benzene contains a closed system of six carbon atoms, and also that hexamethylene is identical with hexahydro-benzene.

Bamberger and Lodter[4] have shown that dihydro-naphthalene gives a dibromide which is converted into naphthalene with the greatest ease. In a later discussion of this case, Bamberger[5] concludes that it is inconsistent with either Dewar's or Kekulè's formula for benzene, and gives the following scheme to show that if we accept either formula, the naphthalene obtained at the end must be different from that at the beginning.



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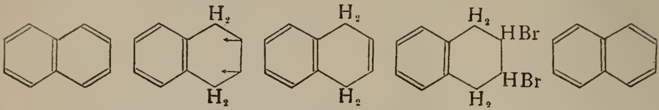
[1] Ber. d. chem. Ges. **19**, 2493, etc., there are eleven or more papers on this subject.
[2] Ibid. **18**, 509, **19**, 308. [3] Ibid. **21**, 1895. [4] Ibid. **20**, 1706. [5] Ibid. **21**, 1903.

In view, however, of the reduction of the $\Delta^{1.3}$ dihydro-terephthalic acid to Δ^{2} tetrahydro-terephthalic acid, the following scheme seems justified.



This leads directly to Kekulè's formula.

In a discussion of the question of double union and of the formation of rings, Baeyer[1] some time ago proposed the following hypothesis as an addition to the Le Bel-Van't Hoff law: "The four valences of the carbon atom are exerted in the directions which join the center of a sphere with the corners of a tetrahedron inscribed within it and, hence, form an angle of 109° 28′ with each other. The direction of attraction can be turned from this normal direction, but a tension is produced in this way which increases as the angle through which the direction is turned increases."

Following this hypothesis, Baeyer shows that the interior angle of the regular pentagon (108°) varies but 1° 28′ from the normal angle for the valences of the carbon atom, while the interior angle of the hexagon is 10° 32′ greater than that of the normal angle. The ring of carbon atoms with five members should, by this reasoning, be the more stable.

If we consider Kekulè's formula in the light of this hypothesis, we find that the angle at each corner of the hexagon is that between the direction of one valence of a carbon atom and the plane of the directions of two other valences.[2] This angle is, normally, 125° 16′, and is only 5° 16′ greater than the interior angle of a hexagon. The tension produced in such a ring should, therefore, be considerably less than that of the hexa-methylene ring. If we consider the geometric forms represented by the formulae of Claus and Dewar and by the "centric" formula, it is evident that the configuration must produce a far greater tension than that of Kekulè's formula.

Not very much weight can be given to such speculations in the present state of our knowledge. The hypothesis seems to gain some support, however, from the marked tendency which has been discovered for benzene compounds to be transformed into compounds containing a ring of five carbon atoms. This tendency is, I believe, always associated with a transformation from the benzene toward the hexa-methylene type. W. A. Noyes.

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[1] Ber. d. chem. Ges. **18**, 2278.

[2] Baeyer himself seems to interpret Kekulè's formula in a somewhat different way. Ann. Chem. (Liebig) **245**, 123.

RECENT RESEARCHES ON COBALT AND NICKEL.

Since the publication, in January last, of the communication by Krüss and Schmidt[1] relative to the occurrence of a new metal in cobalt and nickel, several articles on this subject have appeared in the chemical journals. Krüss and Schmidt, in their investigation, made use of Clemens Winkler's method for the determination of the atomic weights of cobalt and nickel; Winkler therefore does not hesitate to express his opinion in regard to the reported discovery. His article[2] is, in substance, as follows: Having determined, after the appearance of the communication in question, to investigate again the action of cobalt and nickel on a neutral auric chloride solution, he prepares the chloride as follows: 1st, by heating gold in a current of chlorine; 2d, by action of chlorine gas on finely divided gold in water. A solution of the chloride prepared by the first method, when treated with a little sulphurous acid, assumes a deep cherry-red color. This is due to the formation of aurous sulphite, as subsequent analyses of the salt showed that it contained aur*ous* chloride in proportion of 1 molecule $AuCl$ to 23 molecules $AuCl_3$. To use such a substance for the determination of the atomic weight of cobalt and nickel (as Krüss and Schmidt have done) is, of course, inadmissible. On the other hand, the chloride prepared by the second method contains an excess of chlorine—one additional atom of chlorine to every three molecules $AuCl_3$ ($=Au_3Cl_{10}$). He prepares, also, sodium chlor-aurate (the substance used in his own determinations of atomic weights of cobalt and nickel), and the analyses of this show that it contains the gold exclusively in the form of trichloride. The action of cobalt and nickel, says Winkler, on a neutral sodium chlor-aurate solution is a simple one, and there are no secondary reactions. That Krüss and Schmidt should have reached a different conclusion must be due to the fact that they used impure cobalt and nickel. From their description of the action of the metals on the auric chloride solution, he thinks it very probable that the metals contained a small quantity of alkali. Non-reguline cobalt and nickel always show an alkaline reaction. Not only is this the case when the metals are obtained by reduction of their oxides, precipitated by alkalies, but even when obtained by reduction of their oxalates or chlorides, separated from acid solution. Even if the metals are converted into chlorides, and these are reduced anew by hydrogen, they will still show the alkaline reaction, and, strange though it may sound, it appears that even electrolytically precipitated cobalt and nickel may contain alkali. But though this alkali clings to the metals with such wonderful tenacity, investigations, even by spectrum analysis, have not shown with certainty what it is, or in what quantity it is present. If, now, such cobalt or nickel be introduced in a neutral auric chloride solution, what Krüss and Schmidt observed actually takes place. An equivalent quantity of pure gold cannot be precipitated, and the gold always contains either cobalt or nickel, as the case may be. This is not caused by galvanic polarisation, as Krüss and Schmidt supposed, but only by the alkali contained in the cobalt or nickel. Winkler makes a number of similar investigations, always finds cobalt or nickel in the precipitated gold, but in no case is the presence of a third element detected. Cobalt and nickel free from alkali, and perfectly pure, precipitate from neutral auric chloride solution an equivalent quantity of gold free from cobalt or nickel. These metals can be prepared free from alkali and at the same time non-reguline, by sublimation of their pure chlorides in a current of chlorine, and subsequent reduction of the sublimate by hydrogen. It was material prepared in this manner that Winkler used in his atomic weight determinations.

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[1] Ber. d. chem. Gesell. 22, 11.

[2] Ibid. 22, 890.

An article by Dr. Fleitmann[1] is also of interest. The author, having been engaged in the nickel industry for many years, considered it his duty to endeavor to settle the question as to the existence of the new metal. He treats various samples of commercial nickel and cobalt oxides in the manner indicated by Krüss and Schmidt, and obtains negative results in every case. This, coupled with the fact that he had failed to receive a sample of the new metal promised him by Dr. Krüss, causes him to think it probable that the metal exists only in the imagination of its discoverers. Unwilling, however, to confront positive observations with negative results, he refrains from deciding the scientific side of the question, and awaits from Krüss and Schmidt the confirmation or revocation of their communication. In the meanwhile, in order to dispel the alarm occasioned amongst those engaged in the nickel industry, he expresses, in the following terms, his convictions, founded on personal investigations: First: if a new metal really exists, as a regular companion of nickel and cobalt, it is present in extremely small quantities, nothing like 2 per cent. Secondly, such small quantities will have no essential influence on the ductility of nickel, which, in its present purity, is as malleable and ductile as the softest iron. Thirdly, the methods, patented by Krüss for the purification of nickel, are without practical value, as they are in part not new, in part not practical. If, says Dr. Fleitmann, commercial nickel or cobalt, in the form of hydroxide, is treated with large quantities of sodium hydroxide, in the manner described by Krüss and Schmidt, various impurities, such as alumina, lead, zinc and cerium oxides, arsenic, manganic, molybdic, silicic and chromic acids, etc., are dissolved. and, in connection with these, a small quantity (usually not more than $\frac{1}{20}$ per cent. of the oxide used) of nickelous and cobaltous oxides. If the nickelous and cobaltous oxides are separated from the other impurities dissolved in the alkaline extract, they are now found to be insoluble in sodium hydroxide. Hence it appears that their original solubility was occasioned by the presence of those impurities, especially by arsenic acid, silicic acid and alumina. If to the alkaline extract above mentioned, hydrochloric acid be added, until the precipitate that forms is redissolved, and then ammonium carbonate, a wondrous mixture of different oxides and acids is obtained. The author thinks it probable that it was with such a mixture as this that Krüss and Schmidt had to deal.

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[1] Chemiker Zeitung **13**, 757.

The investigation of Krüss and Schmidt is far from complete as yet, but they have very recently made a short communication[1] relative to its progress. Having obtained, after the most careful purification, a specimen of nickel in which no known impurity can be detected, they endeavor to ascertain the equivalents of the two oxides into which nickel oxide can be separated. This separation is effected by methods previously described by them, as well as by fractional precipitation of basic nickel-ammonium arsenite. Determinations of the atomic weights result as follows: For the metal of lower atomic weight 56 to 58. For the metal of higher atomic weight 61 to 100. Hence the atomic weight of the former appears to be somewhat lower than the atomic weight of nickel, as at present accepted, and that of the latter considerably higher. After these determinations the metals are subjected again to an exact qualitative investigation, which convinces the authors that they contain no known impurities which, in the one case, would tend to lower the atomic weight of nickel, or, in the other, would tend to raise it. These results confirm their former supposition as to the compound nature of nickel; still it is at present doubtful whether it is a mixture of two or of several metals, and hence they refrain from a discussion of the relation of the atomic weights of the two portions to the periodic system. Consideration of Mr. Winkler's article is reserved for a later and more extended communication.

C. C. BLACKSHEAR.

A TREATISE ON THE PRINCIPLES OF CHEMISTRY. By M. M. Pattison Muir, M. A., F. R. S. E., Fellow, and Prælector in Chemistry, of Gonville and Caius College, Cambridge. Second Edition. Cambridge: University Press. 1889. 490 pp. 8vo.

In the first edition of this book Mr. Muir made an earnest effort to treat the general principles of chemistry in a scientific way, and in many respects he was markedly successful. The book, however, lacked clearness. It was by no means an easy matter always to tell what object the author had in view, and the relations between the different parts could not be clearly recognised. It is evident that the author himself was conscious of this defect, and he has attempted to remedy it. In the preface to the second edition he says: "The aim and scope of the book have not been changed. The whole has been thoroughly revised, and Book II has been entirely rewritten. The revision will, I hope, make clearer than before the mutual dependence of the parts.

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[1] Ber. d. chem. Ges. 22, 2026.

"Since the first edition was published, much important work has been done on subjects treated in Book I; the results of this work have been noticed in the present edition; at the same time some chapters have been shortened, especially that dealing with valency and isomerism; the arrangement of these, and some other chapters has been altered. The chapters on physical methods have been rewritten.

"When the first edition was published, the study of chemical affinity was entering on a new phase; since 1884 progress has been very rapid, and to-day we are much nearer the goal than we were five years ago. The great importance of recent work on affinity has compelled me entirely to rewrite Book II. In doing this I have largely followed Ostwald's *Lehrbuch der allgemeinen Chemie;* without that admirable treatise, the part of my book dealing with affinity could not have been written. I am anxious to express, as strongly and warmly as I can, my indebtedness to Prof. Ostwald."

A careful examination of the new edition shows that the revision does in fact "make clearer than before the mutual dependence of the parts." The book is in every way an improvement upon the first edition, and it will no doubt find a larger field of usefulness.

The author's attempt to frame an unassailable definition of valence leads him to the following: "*The valency of an atom is a number which expresses the maximum number of other atoms between which and the specified atom there is direct interaction in any gaseous molecule.*" This definition would seem to be too narrow. It is certainly simpler to restrict the conception to gaseous molecules, and the results are more trustworthy, but surely there are cases in which the study of composition, taken together with that of chemical transformations, can lead to conclusions of value with regard to the subject of valence. If it is found that by making a simple assumption a large number of otherwise wholly incomprehensible chemical reactions can be explained, it is just as well for the time being to make the assumption, and then see what comes of it. But we must of course not forget that we have made the assumption. There is great danger that we shall forget it, but that is true of every working hypothesis, and yet we cannot do without them. It would simplify chemistry very much indeed if all compounds and all elements could, without decomposition, be converted into perfect gases. We have to take things as they are. In spite of objections which can be raised, however, Mr. Muir's caution is wholesome, and the lesson he is teaching is loudly called for. In regard to the objection above mentioned, the author says (p. 243): "But it may be urged that a much wider meaning ought to be given to the term valency. Better, I would reply, employ another term or other terms. Let us make as much use of valency as we can; so far as it goes it is definite, without it the chemistry of carbon compounds especially could not have made the advances which it has made. But it is not all." It is difficult to see how the introduction of another term or other terms would help the matter. Before we can hope to gain a satisfactory knowledge of valence it is necessary that we should group together the phenomena of valence. Now it would seem that the introduction of new terms for the purpose of designating some of these phenomena would hinder rather than further progress.

It should be said that the point which is here criticised is of minor importance as far as the book is concerned. There is, further, room for an honest difference of opinion, and it is well for chemists that the subject of valence should be presented to them from the author's point of view. Radical treatment is necessary in many cases.

Book II which, as the author distinctly tells us, is based upon Ostwald's *Lehrbuch der allgemeinen Chemie*, is clearly written and will be of great service to students. Whatever may have been the case a few years ago, it is certainly true now that no chemist can afford to be without a knowledge of the recent developments in the study of affinity. These developments are unquestionably among the most important that chemistry has to show of late. The most recent results have been incorporated in the book, and it can be cordially recommended to students.

I. R.

WATTS' DICTIONARY OF CHEMISTRY. Revised and entirely rewritten by H. FOSTER MORLEY, M. A., D. Sc., and M. M. PATTISON MUIR, M. A., assisted by eminent contributors. In four volumes. London and New York: Longman, Green & Co., 1888, 1889. Price $14.50 a volume.

The first edition of this work was published twenty-five years ago. It appears from the preface of the new edition that "some time before his death Mr. Watts had agreed to prepare a new edition of his dictionary, which should give as complete an account of the present state of the science as might be found compatible with the appearance of the book in four volumes of 750 pages each." After the death of Mr. Watts the work planned and begun by him was taken up by the present editors, and two volumes of the dictionary have already been published. In order to keep within the prescribed limit of four volumes a very condensed style has been adopted, abbreviations are freely used, and formulae are frequently employed instead of names. Further, the new edition treats of chemistry only, whereas the old edition had to deal also with "the allied branches of other sciences." No special information is given with regard to chemical technology, though "technical chemistry will be treated in a companion volume to be published under the editorship of Professor Thorpe." Details in regard to analytical processes have, in general, been omitted. The free use of abbreviations throughout gives the pages a confused appearance, but it requires only a little practice to enable one to read the matter readily. Although the number of organic compounds has doubled since the appearance of the first edition, "nevertheless the space allotted to them in the present dictionary is little more than quarter of that devoted to organic chemistry in the original dictionary and its supplements." Besides the articles on special subjects, there are many on general subjects. Among those in the first volume which are worthy of special note are the following: Allotropy, by Lothar Meyer; Affinity, by W. Ostwald; Acids and Alloys, by W. Ramsay; States of Aggregation, by J. J. Thomson; Bacteria, by E. Ray Lankester; Chemical Change, by J. J. Hood; Azo-coloring Matters, by Raphael Meldola; Atmosphere, by T. E. Thorpe; Ash of Organic Bodies, by R. Warington; and Atomic and Molecular Weights, by Mr. Muir. In the second volume the following are of special importance: Chemical Equilibrium, by J. J. Thomson; Dissociation and Explosion, by R. Threlfall; Elements, by F. W. Clarke; Combustion and Flame, by T. E. Thorpe; Crystallisation, by Harry Baker; and Laws of Chemical Combination, by Mr. Muir.

The names of the editors and of the special contributors give us confidence in the accuracy and thoroughness of the book, a confidence which is strengthened by an examination of a number of the articles. It appears that in the new Watts' Dictionary chemists have an extremely valuable, compact work of reference which must become a necessity in every well-stocked chemical library.

I. R.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By A. BERNTHSEN, Ph. D. Translated by GEORGE McGOWAN, Ph. D. London: Blackie & Son, 1889; and New York: D. Van Nostrand Company, 1889.

The original book, of which this is a translation, is considerably smaller than Richter's well known treatise on the same subject, and is intended for those who are in the early stage of their study of organic chemistry. It is clearly written, and must be helpful to students who have already acquired some knowledge of the compounds of carbon. For the beginner it contains too much, as is the case with nearly all so-called elementary treatises on the subject. Its use should be preceded by that of some still smaller book, in which stress is laid upon the system rather than on the properties of individual compounds. With some knowledge of this system, the student can then proceed with advantage to a more thorough study of the subject as it is presented in this book.

The translation is not entirely satisfactory, though it is better than most translations of German books on chemistry. The following curious passage occurs on p. 15: "With the setting up of the type CH_4 by Kekulé, and the knowledge of the tetravalent nature of carbon accompanying this, were connected the endeavors of Kolbe to derive the constitution of organic compounds from carbonic acid, but from an incomplete grasp of the subject of equivalent proportions a clear insight into this was not arrived at." It is a little difficult to see exactly what is meant by this, but one thing is clear, and that is that Mr. Bernthsen thinks Kolbe had "an incomplete grasp of the subject of equivalent proportions." The student who may use the book is advised to read the original papers on the subject referred to, before coming to the conclusion that Kolbe had an incomplete grasp of it.

I. R.

A Manual of Assaying Gold, Silver, Copper and Lead Ores. By Walter Lee Brown, B. Sc. Third Edition. Chicago: E. H. Sargent & Co., 1889.

This book, to quote from the preface, "is written as a guide to those who having had no previous technical or especially scientific education, desire to learn something of the practical assaying of gold and silver ores." It is an excellent book; clear and concise, it covers all the practical difficulties which the beginner meets. It can be especially recommended to chemists, who will find that backed by their knowledge of the chemical changes involved in assaying, they need no further help to become good assayers with practice.

E. R.

NOTES.

On the Separation of Copper from Cadmium.

The two methods which are in use at present for the separation of these two substances, while they are both good and efficient in the hands of experienced persons, nevertheless present some difficulties when placed in the hands of the beginner. The best one, and the one generally given in most books on qualitative analysis, depending on the difference in conduct of the double cyanides of copper and cadmium towards hydrogen sulphide, is objectionable, for the reason that it involves the use of potassium cyanide, a substance the use of which by the average young student had better be avoided unless he is under the constant supervision of the instructor. My own experience as a teacher has shown me also that in the hands of those just beginning the study of qualitative analysis, the other method, depending on the difference in the solubility of the sulphides of these two metals in dilute sulphuric acid, is far from yielding satisfactory results.

The following simple method involves the use of no reagent which would be likely to prove harmful, and it has given good results even in the hands of very unskilled persons. The method depends upon the fact that metallic iron precipitates the copper completely from solutions containing copper and cadmium and leaves the cadmium in solution.

The method of procedure is as follows: The filtrate from the bismuth, if seen to contain copper either by its blue color or by giving the characteristic red color with potassium ferrocyanide in the presence of acetic acid, is acidified with dilute nitric acid and evaporated to dryness, and the residue heated until the nitrates are decomposed. The mass is then treated with a few drops of concentrated hydrochloric acid, and the solution diluted with about five times its bulk of water and filtered into a test tube. Metallic iron (fine piano wire is a good form to use) is now added to this filtrate, and the tube and its contents are then heated in a water-bath until the solution is perfectly colorless. The temperature of the bath need not exceed 80° C., and the solution containing the chlorides of copper and cadmium should be acid enough to cause a slow evolution of hydrogen at this temperature. Under these conditions the copper is rapidly precipitated on the iron, and I have generally found that an hour's heating on the water-bath is sufficient to precipitate all of the copper, even when present in comparatively large quantity. When the precipitation of the copper is complete, the colorless solution is filtered from the copper and the excess of iron, diluted with an equal quantity of water and treated with hydrogen sulphide. A yellow precipitate indicates cadmium. The copper can be easily recognised by the red color of the precipitate on the iron, but, of course, the presence or absence of this substance must be inferred from the color of the filtrate from the bismuth.

The satisfactory results obtained by this method lead me to believe that instructors will find it to their advantage to use it with students who who have had but little experience in laboratory work.

J. H. Kastle.

Lexington, Ky., *October*, 1889.

Decomposition of Potassium Chlorate by Heat in the presence of Manganese Dioxide.

In view of the obscurity of the knowledge in regard to the cause of the ready decomposition of potassium chlorate when heated in the presence of manganese peroxide, an investigation of the subject was undertaken by Herbert McLeod.[1]

The experiments were conducted in a very simple manner. The mixture of potassium perchlorate and manganese peroxide was placed in a small test tube connected with a U tube containing a solution of potassium iodide. The test tube was then placed in a larger test tube containing mercury, and this was heated until the vapor of the mercury rose above the mixture in the small tube, corresponding to a temperature of about 358° C. The oxygen liberated was determined by difference in weight before and after the operation, less the weight of chlorine evolved. This last displaced the iodine in the solution of potassium iodide, and its amount was determined by titration with sodium thiosulphate. Various kinds of oxides of manganese were used in the experiments; and several of the experiments were viewed through a microscope.

As a result of these experiments, McLeod concludes that the reaction takes place as follows: In the first place, the potassium perchlorate and manganese peroxide react upon each other, forming potassium permanganate, and liberating chlorine and oxygen, thus

$$(1) \qquad 2KClO_3 + MnO_2 = K_2Mn_2O_8 + Cl_2 + O_2.$$

Under the influence of heat the permanganate is then decomposed into potassium manganate, manganese peroxide and oxygen, thus:

$$(2) \qquad K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2.$$

Finally the manganate so formed is attacked by the chlorine, giving potassium chloride, manganese peroxide, and oxygen.

These conclusions are based upon the following observations: in regard to (1), he found that chlorine is undoubtedly given off in the early stages of the reaction, and that if some substance which will take up chlorine, for example sodium carbonate, be added to the mixture, the decomposition is incomplete. After this action permanganate was found in the mass. He also noticed that if a small quantity of peroxide be used, the fused mass is pink, and if this is now heated in mercury vapor, the color remains until all the potassium chlorate is decomposed, then turns green and finally brown. Now if this pink color is due to permanganate, then the latter is being continually formed, because if potassium chlorate and potassium permanganate are heated together, the permanganate is decomposed between 250° and 275° C. The fact that the permanganate decomposes at this temperature is proof of the second stage of the reaction (2).

The evidence in favor of (3) is based upon the fact that when the reaction is complete a black powder is found sticking to the sides of the tube. This is probably regenerated manganese peroxide. Moreover, when chlorine is passed into the mass resulting from the fusion of potassium permanganate, the chlorine is absorbed and oxygen is given off. At ordinary temperatures both potassium chloride and manganous chloride would be formed, but at the temperature of mercury vapor manganous chloride is decomposed, yielding an oxide of manganese and chlorine.

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[1] J. Chem. Soc., April, 1889.

In addition to these facts, McLeod shows that with very small quantities of manganese peroxide the action is complete, but takes place much more slowly, and that the same peroxide can be used repeatedly for a similar purpose, but it changes in appearance from brown to black, showing that it has taken part in the chemical action and has been reproduced. A bright crystal of pyrolusite used in one experiment was changed to needle-shaped fragments. An interesting experiment was made to determine whether the peroxide served only for supplying nuclei for gas evolution. To this end platinum black, a chemically inert substance, was substituted for the peroxide and the experiment conducted as before. The reaction took place to a limited extent only. He concludes from several observations made with the microscope, that only a portion of the manganese peroxide is changed, the rest acting as nuclei for gas evolution.

CHAS. H. HERTY.

Some Modifications of the Kjeldahl Method for Estimating Nitrogen.

Several modifications of the Kjeldahl method for estimating nitrogen have recently been published. F. Martinotti[1] finds that, in case no nitrates are present in the substance to be analysed, the original method of Kjeldahl gives results which agree amongst themselves and compare very favorably with the results obtained by the method of Dumas.

In case nitrates are present, however, neither the original Kjeldahl method nor Jodlbauer's modification (*i. e.* where phenolsulphonic acid is used) gave good results. The percentage of nitrogen was always found to be too low, and varied with the length of time during which the heating was continued. It was found best to estimate the nitrogen which was in the form of nitrates by Schlösing's method (*i.e.* by the use of ferrous chloride and hydrochloric acid). The nitrogen in other forms than nitrates is best estimated as follows: The weighed substance is treated with ferrous chloride and hydrochloric acid and evaporated to dryness, thereby eliminating the nitrates. The nitrogen in the residue is then estimated by the plain Kjeldahl method.

O. Foerster[2] also finds that neither the original Kjeldahl method nor the modification in which phenolsulphonic acid is used gives accurate results. All of the nitrogen of nitrates is not converted into ammonia, and the results, consequently, are too low. He finds that sodium thiosulphate converts nitric acid into nitrosyl-sulphuric acid, thus:

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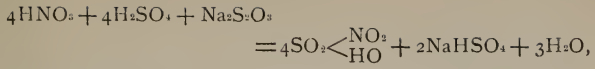
[1] Ztschr. anal. Chem. 28, 415.

[2] Ibid. 28, 422.



$$4HNO_3 + 4H_2SO_4 + Na_2S_2O_3 = 4SO_2<\begin{smallmatrix}NO_2\\HO\end{smallmatrix} + 2NaHSO_4 + 3H_2O,$$

and nitrosyl-sulphuric acid is readily converted into ammonia. He therefore recommends that sodium thiosulphate be added to the contents of the digestion flask after the action of the phenol-sulphonic acid has continued for some time. In this way good results are obtained.[1]

J. W. Gunning[2] finds that the addition of potassium sulphate to the sulphuric acid which is used in the plain Kjeldahl method greatly facilitates the complete oxidation of the organic matter. In the unmodified method the sulphuric acid gets so weak towards the end of the operation, from the loss of sulphur dioxide and from dilution by the water formed in the reaction, that the oxidation proceeds very slowly. By the addition of potassium sulphate to the sulphuric acid, potassium acid sulphate is formed, and this gives up water rather than sulphuric acid. In the process of heating, therefore, the water is constantly distilled off, and the acid, instead of getting weaker, gets stronger. By this method the complete oxidation of the substance, until the contents of the flask are perfectly colorless, is generally effected in from ½ to 1 hour, and never takes more than 2 hours with the most difficultly oxidisable substances.

R. DE ROODE.

A Simplified Fat-Extracting Apparatus.

The Soxhlet extracting tube, notwithstanding its effectiveness, is nevertheless open to objections on account of its complicated construction and consequent expense. When one of the small tubes is broken the whole instrument is rendered useless.

Recently, while conducting some analyses under Mr. Walter Maxwell in the Harvard Chemical Laboratory, it occurred to me that this apparatus could be simplified without detracting from its effectiveness. The apparatus which I devised consists of three pieces :

1. A piece of glass tubing 4 cm. wide and 20 cm. long is drawn out at one end so as to pass through a rather large hole in a cork.
2. A large-sized test-tube is fitted into the larger tube so as to come within 3 cm. of the top.
3. A glass tube of small bore, best about ⅓ cm. bore, is bent in such a way that one end reaches to the bottom of the inner test-tube, while the other goes between the inner and the outer tubes and reaches into the part of the outside tube that has been drawn out. This end can be slightly bent so as to accommodate itself to

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[1] *Note by Abstracter.*—No mention is made either by Martinotti or Foerster of the modification of M. A. Scovell, of the Kentucky Agricultural Experiment Station (*i. e.* where salicylic acid is used in the place of phenol), which, in the case of potassium nitrate, gives remarkably accurate results.

[2] Ztschr. anal. Chem. **28**, 188.

the outside tube. To set the apparatus up, hang the bent tube over the top of the larger of the two large tubes, and place these in the piece first described. The bottom of the latter is connected with a small flask, while the upper portion is connected with a condenser. The substance under examination is placed in the inner tube after having been wrapped in a piece of filter paper. As soon as the distillation begins, the ether or alcohol passes from the flask through the outside tube, is condensed, and falls into the inner tube. Just before the inner tube has become filled, the capillary attraction draws the liquid through the siphon, and the whole liquid contents with the extracted fats are siphoned into the flask below.

At first I had some difficulty in getting the apparatus to work satisfactorily because of the inner tube settling down below the top of the siphon, but with a little care this difficulty can be avoided. I have used several of these extractors with satisfactory results. The apparatus is very easily constructed out of ordinary glass tubing. It certainly has two characteristics to recommend it, viz. simplicity and neatness. J. T. CRAWLEY.

International Congress of Chemists.

An International Congress of Chemists was held in Paris during the past summer. Many questions of interest were discussed, and it was finally decided to appoint an International Commission to consider the subject of chemical nomenclature. The commission consists of: Messrs. Berthelot, Friedel, Béhal, Bouveault, Gautier, Schützenberger, Grimaux, Jungfleisch, Fauconnier, Combes (France); Graebe (Switzerland); Alexeieff, Beilstein (Russia); Baeyer, Nölting (Germany); Lieben (Austria-Hungary); Franchimont (Holland); Paterno (Italy); Armstrong (England); Istrati (Roumania); Ira Remsen (United States); Calderon (Spain); Bonkowski-Bey (Turkey); Cléve (Sweden); Mourgues (Chili). An abstract of the proceedings of the meeting of the Congress will be given in a later number of this Journal.

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Contributions from the Chemical Laboratory of Harvard College.

LXIV.—ON A NEW METHOD OF DETERMINING GAS DENSITIES.[1]

By JOSIAH PARSONS COOKE.

In the well known method employed by Regnault for determining the density or specific gravity of air, oxygen, nitrogen, hydrogen, and carbonic acid, we deal primarily with tares, of which the weights to be determined are the differences. The glass balloon which holds the gas is tared by a similar balloon of exactly the same volume and of nearly equal weight, suspended from the opposite pan of the balance. The small difference of weight required to establish perfect equilibrium is alone measured with standard brass or platinum weights. Whatever may be the form of the subsequent calculation, the primary object is to obtain the tare of the empty balloon when absolutely vacuous. This known, the differences between such tare and the tare of the balloon filled with various aeriform substances, gives the weights of equal volumes of these substances under the temperatures and pressures at which the balloon was filled. The volume of the counterpoise is exactly adjusted to that of the balloon by the aid of a small subsidiary glass bulb (Plate II); and by sealing up more or less mercury in this bulb it is easy to make the difference of weight such that the standard weights required to complete the equilibrium will measure the differences of tare to be determined, and no more.

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[1] From the Proceedings of the American Academy of Arts and Sciences.

In the method of Regnault the tare of the empty balloon, or what was equivalent to it, was found by exhausting the balloon with an air-pump and weighing it after measuring the tension of the residual gas while the glass was surrounded by ice. But it has been shown by Agamennone[1] and Lord Rayleigh[2] that the results thus obtained are vitiated to a small extent by the circumstance that when the balloon is exhausted the pressure of the atmosphere determines a slight shrinkage of the external volume, which naturally disturbs the exactness of the compensation between the buoyancy of the air on the balloon and on its counterpoise. Although this shrinkage can be readily measured, as was done by Dr. T. W. Richards under my direction,[3] and still more recently by Professor Crafts,[4] who experimented on the balloon used by Regnault, which fortunately has been preserved, it seemed desirable to develop a method by which this correction could be avoided. For even if the new method should lead to no more accurate results than before obtained, it might serve to confirm the validity of the correction in question, and at least would give additional data towards establishing the value of important physical constants.

The new method we have devised for the purpose consists in first taring the balloon when filled with carbonic acid gas, and then drawing the gas through absorption tubes and determining its weight, as in the well known method of organic analysis. This weight known, the tare of the empty balloon is obviously the difference between the first tare and the weight in question. The practical problem here presented is, however, far more difficult than that of organic analysis. In the last we expect to determine the weight of only a few decigrams of carbonic acid within a few tenths of a milligram, while in the problem now before us we must weigh at least nine or ten grams of carbonic acid, not simply to a proportional, but to an equal, degree of accuracy. We only succeeded in securing such accuracy after many trials and a careful study of all the conditions involved, and our primary object in this paper will be to describe the precautions which are essential to the success of the new experimental method. Incidentally it will appear that our results confirm in a most striking manner the high value of the specific gravity of hydrogen found by Lord Rayleigh,[1] and the low value of the atomic weight of oxygen found by ourselves.

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[1] Atti (Rendiconti) d. R. Accad. dei Lincei, 1885.

[2] Proceedings of the Royal Society **43**, 362 (1888).

[3] This Journal **10**, 191 (1888); and Proceedings Am. Acad. **23**, 177 (1888).

[4] Comptes Rendus **106**, 1662 (1888).

The Balance and Weights.

The balance and weights were the same as those used by us in our previous work.[2] The disposition of the apparatus which, after many trials, we have found most suitable for accurate work, is shown in Plate II. The balance rests on the plank shelf of a wooden case, whose glazed doors are shown open in the drawing; and as this shelf is firmly secured to a thick brick partition wall behind, great steadiness is secured for the instrument. Around the inside of the wooden case are hung folds of drapery, which surround the balance case and protect the beam from radiations, while a curtain rolling on a spring fixture enables the experimenter to uncover the front as necessary. Fastened by flanges and screws to the under side of the same shelf is a box made of tinned sheet iron, of somewhat larger dimensions than the balance case. The front of this box can be almost wholly uncovered by means of two large doors made of the same metal sheet, and secured when closed by turning buttons, but shown open in the drawing. In the metal top are two circular holes about half an inch in diameter, corresponding to holes through the shelf and the base of the balance case, and directly under the centers of the balance pans. From hooks soldered to the under side of the pans the globe and its counterpoise are suspended by means of brass wires, and the lengths of the wires are so adjusted that the two glass vessels shall hang midway in the metal box. The globe is hung from a wire stirrup (Plate I), which swings from an eye at the end of one wire; while on the neck of the counterpoise is cemented a brass cap and hook, and both it and the small subsidiary bulb are hung on an eye at the end of the other wire. Of course these details might be varied. It is only important that the whole system should swing freely, with as little friction as possible, and that the balloon should be easily removed and replaced.

Through a third hole in the top of the metal box and shelf, placed just in front of the balance case, passes a thermometer (not shown in the drawing) by which the temperature may be watched, and the inside of the box is painted with lamp-black so as to secure a uniform temperature throughout the interior. In our previous paper we spoke of the disturbance sometimes caused by currents of air within the box, but we found on further experience that these currents could be prevented by keeping the interior of the box as nearly as possible at the temperature of the external air. For this purpose it is important that the air of the room should circulate as freely as possible around the box, and the required condition is more easily secured if the box is made of thin metal sheet. It is also important that the temperature of the room should not be constantly changing, and that all circumstances should be avoided which would cause a flow of heat either into or out from the box. Sitting in front of the box in the process of weighing immediately causes a disturbance, and hence the division of the outer wooden case below the shelf is provided with wooden doors, which should be shut in front of the metal box before approaching the balance. When the thermometer hanging with its bulb inside the box indicates the same temperature as one hanging from the balance case outside within one-tenth of a centigrade degree, the conditions are most favorable for accurate weighing.

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[1] Proceedings of the Royal Society **45**, 426 (1889).

[2] This Journal **10**, 92 (1888); and Proceedings Am. Acad. **23**, 159 (1888).

In order to maintain the atmosphere within the box in a constant hygrometric condition, we placed in it four large open dishes of sulphuric acid, two on the bottom of the box and two on a shelf near the top, as described in our previous paper. The acid was first boiled with a fraction of a gram of ammonic sulphate, to remove the last traces of nitrous fumes, and renewed as occasion required.

We have found that we can most accurately estimate slight differences of weight with a balance thus loaded by observing the amplitude of the first swing of the pointer when the pans are relieved. With the balances of Becker, after the beam has been set on its bearings by the usual cam motion, the pans are still supported by two delicate arms, which are held by a weighted lever against the under side of the pans, but which can be pressed down by pushing against the button shown in the drawing on the front of the balance case. Such a mechanical arrangement is peculiarly adapted to this method of weighing, as it relieves the pans suddenly and under the same conditions, so that the amplitude of the subsequent swing is an accurate measure of the difference of weight acting at the two ends of the balance beam; and in this case the inertia of the heavy load renders the effects surprisingly uniform. We give these details, not because they involve any new principles, but because the results have been reached after a long series of experiments, and our experience may save others much loss of time. With the apparatus arranged as we have described it, a difference of weight amounting only to one-tenth of a milligram was distinctly indicated, although the load exceeded half a kilogram on each pan, and the compensation was made so perfect that the equilibrium was not perceptibly altered by any ordinary changes of atmospheric conditions.

In order to reach such compensation, a counterpoise is first selected, which, on rough measurement, appears to be nearly of the same volume as the balloon, and at the same time a little lighter in weight. The apparatus is then mounted with this counterpoise as described, the stop-cocks of the balloon being closed. A series of observations are then made of the variations of weight arising from changes of atmospheric pressure and temperature, as carefully measured as possible. From such observations we can readily calculate, by the method we have previously described,[1] the volume of the small bulb required to make the compensation perfect, and an experienced glass-blower can readily make a bulb of the size indicated, which, before it is sealed, may be adjusted as to weight by loading with mercury as above described.

The weights used in connection with the balance had been adjusted for our previous work with the greatest care, and not only compared with each other, but also compared with a copy of the Washington standard. Although we shall deal in this paper solely with relative weights, yet the absolute values that may be deduced from our results must be correct far within the limits of the experimental errors of our own work. The sum of the weights required to measure the differences of tare never exceeded twelve grams, and of this small mass any possible difference between our copy and the Paris standard kilogram must be wholly inappreciable.

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[1] Proceedings Am. Acad. **18**, 55.

The Glass Balloon.

We have used in this investigation the same glass balloon that was fitted up for a somewhat different purpose in our work on the atomic weight of oxygen, but which has proved equally well adapted to determinations of gas density. Regnault in his work on the same subject used a balloon of ten liters' capacity, having its neck closed with a brass cap and stop-cock, and filled it by alternately exhausting the interior with an air-pump and refilling from a gasometer until the complete purity of the enclosed gas was assured. After long experience with this mode of experimenting, we have found it more convenient to fill the balloon by displacement directly from the generator, and we have found that we can reach a satisfactory result with least labor in this way.

Our balloon is represented in Plate I, which shows all the details of its construction. It was made by Emil Greiner of New York, and all the joints are so finely ground that when properly lubricated they will hold a vacuum indefinitely. The peculiar form of the stop-cocks enables the experimenter to shut into the globe a definite volume of gas and at the same time open a vent to the generator through the side tube; or to allow the gas to flow through the side tube until the current is perfectly pure before it is admitted to the balloon; and again, when the stop-cocks are both closed and the balloon disconnected, all the gas left in the connecting tubes will soon be replaced by air. At the freezing point the internal volume of the balloon, as nearly as we have been able to measure it, is 4961.5 cubic centimeters, and the weight of the glass 570.5 grams. After much experimenting, we have concluded that as great accuracy in determinations of gas density can be obtained with a balloon of this size as with a larger one. The advantage to be derived from the greater mass of gas experimented on is more than compensated by the greater liability to error which the weighing of larger vessels and the longer duration of all the processes involve.

The extent to which this balloon is actually compressed by the tension of the atmosphere when a vacuum is made in the interior has been carefully measured,[1] and amounts to 1.66 cubic centimeters for a difference of tension of 760 mm. between the interior and exterior of the glass vessel; and this corresponds to a loss of buoyancy of 1.96 milligrams in the air at 760 mm. and 22° C.

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[1] This Journal **10**, 193 (1888); and Proceedings Am. Acad. **23**, 182 (1888).

When the balloon was not hanging on the balance, it was always protected by a metal case (see Plate II), from which the neck and connecting tubes alone protruded, and in transferring the balloon to and from the balance it was handled only by the neck.

In Regnault's experiments the balloon was filled with the gas under examination at the temperature of 0° C. by surrounding the glass with melting ice. This necessitates a careful cleaning of the globe at least twice during each determination, and thus may arise slight variations of condition to impair the accuracy of the results. We have found with Lord Rayleigh that it is preferable to fill the balloon at the temperature of the laboratory, but we must then observe the temperature with very great accuracy. It is important to know the temperature to the one hundredth of a centigrade degree, for even so small a difference of temperature as this causes a change in the amount of carbonic acid gas which our balloon will hold under ordinary atmospheric conditions corresponding to three tenths of a milligram.

We have found it possible to secure even such constancy of temperature as this delicate measure implies by placing the balloon while filling in a calorimeter case, and observing the temperature with a calorimetric thermometer divided to the fiftieth of a centigrade degree. The calorimeter case consists of a cylindrical vessel of sheet zinc wide enough to receive the balloon with its tube and leave a play of less than an inch on either side. This vessel is fastened by metal stays inside a second cylindrical vessel of the same material, leaving an annular space about two inches wide and an equal space between the bottoms of the two vessels, all of which is filled with water. In addition, the outer vessel is further protected by a layer of felt one inch thick, kept in place by an outer covering of the same sheet metal. When in use, the top is covered by a cap made also of thick felting, and in the crown of the cap is a slit, through which a thermometer may be inserted or the hand passed to turn the stop-cocks. The gas to be used is conducted into the calorimeter through a very small lead tube, which is connected with the lower tubulature of the stop-cock by a rubber connection, and the balloon is so placed that the current shall enter either at the top or at the bottom of the vessel, according as the gas is lighter or heavier than the atmosphere. The calorimeter case stands about four feet high, and the balloon rests in it on a down cushion, with the connecting tubes fully six inches below the surface of the water in the annular space above mentioned. With this apparatus it was possible to keep the temperature of the balloon constant within the one hundredth of a centigrade degree for an hour at a time, unless the temperature of the laboratory suddenly and greatly changed.

The general arrangement for filling the balloon was then as follows. The gas delivered from the drying tubes of one of the generators hereafter to be described passed through the lead tube of which we have spoken to one or the other, as the case might be, of the tubulatures of the balloon standing in the calorimeter. Passing out by the opposite tubulature, the current was conducted by a similar lead tube to a second but much larger balloon serving as a gasometer, and from the last vessel through a gas wash-bottle to the atmosphere. The bottom of the wash-bottle was covered with strong sulphuric acid to dry any returning air, but not deep enough for the inlet tube to dip under the liquid. The current was continued until the proper test showed that the gas issuing from the end of the apparatus was perfectly pure. Then the inlet cock of the balloon was turned, and the temperature of the calorimeter case watched until constant, and a sufficient time had elapsed to establish a perfect equilibrium with the atmosphere through the connecting tubes and vessels. This, as we found by experience, often requires longer time than we were led to anticipate, and when experimenting with carbonic acid gas it is not safe to allow less than twenty or thirty minutes; and now the large balloon and wash-bottle come into play to prevent air diffusing into the balloon, or being drawn back in consequence of changing pressure.

When all the conditions seemed to be satisfactory, the temperature of the calorimeter and the height of the barometer were accurately observed, the first to the hundredth of a centigrade degree and the last to the twentieth of a millimeter, noting always the height of the attached thermometer. The hand was then quickly thrust into the calorimeter, and the outlet cock at once closed. The balloon was now removed, dusted with a large camel's-hair brush, and hung in its place on the balance. When, however, the atmosphere is very dry, as it often is in this climate during the winter months, it may happen that the surface of the glass acquires a charge of electricity from the friction of the cushion in the calorimeter or of the brush just mentioned; and if there is any suspicion of such an effect, the best way to dissipate the charge is to stand the balloon for a few minutes in its metal case (shown in Plate III), after covering the bottom of the case with a thin layer of water. If the balloon is hung on the balance with a charge of electricity on its surface, however small, it will be unequally attracted by the surrounding metallic walls, and most confusing anomalies of weight will be noticed. Moreover, in the very dry atmosphere of the case the charge will last for days, or even weeks, as on the insulated vanes of an electrometer.

Thermometers and Barometers, and their Correction.

The thermometers on whose indications we have relied in this investigation are two of small range, but divided into fiftieths of a centigrade degree and made by the house of the late Dr. H. Geissler of Bonn. We were obliged to use the two, for our investigation was continued into summer weather, which exceeded the range of the thermometer first selected. As should always be the case with such instruments, the zero point is given in each case on a short subsidiary scale, separated from the main scale by an enlargement of the tube. Careful observation showed that the zero point of the instrument we will designate as No. 1 was depressed 0.02 of a centigrade degree, while the zero point of No. 2 was raised 0.28 of a degree. Making the correction thus indicated, to be added to all temperatures observed with No. 1, and subtracted from all observed with No. 2, the two instruments were found to agree exactly through all portions of the scale common to both. Obviously, therefore, the differences of temperature observed are perfectly trustworthy to the one hundredth of a degree, but how far the absolute values—counting from the freezing point of water—can be relied on when compared with the observations of other experimenters, we have no means of determining. Of course, it will be understood that all temperatures hereafter given have been corrected for the variation of the zero point. At the close of the investigation the zero points were again tested and found to be unchanged.

The barometer used was a large standard instrument of the familiar mountain form, made by Greene of New York. Hanging at the side of it was a smaller instrument of the same maker, whose indications agreed with the first within the tenth of a millimeter. Here again, as in the case of the thermometer, there can be no question as to the accuracy of the differences of tension observed within moderate limits; but how far the absolute heights can be compared with those observed by Regnault and others is also a problem that cannot be readily solved, and one not within the means of a single experimenter to determine. All heights of barometer given hereafter have been reduced to 0° by the tables of Guyot.[1]

Tare of the Empty Balloon by Regnault's Method.

In the method of experimenting devised by Regnault the tare of the empty glass globe used, although not explicitly given, was implicitly determined. His arrangement for filling the globe, shown by Figure 1, has already been referred to, and his general method of experimenting consisted in taking the tare of the globe when filled with the same gas at the temperature of melting ice under as different tensions as possible. The tensions were found by measuring with a cathetometer the difference of height, $\alpha\ \beta$ (see Fig. 1), under each condition, and the tares were found by means of the balance by the system of compensation already described. The difference of tare gives the weight of gas which the globe contains at 0° at the tension $H—h$, and from this may readily be deduced the weight at any other tension; as, for example, at the standard tension of 760 mm. The calculated weight at either of the tensions H or h, deducted from the corresponding tare, gives what we have called the tare of the empty globe; but obviously with Regnault's method this value is not needed in the calculations of specific gravity or density.

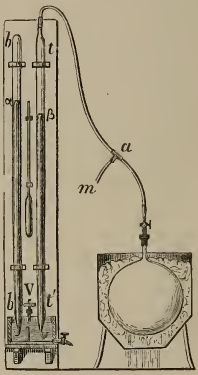

FIG. 1.

When the globe is filled by displacement it conduces to greater accuracy to determine independently the tare in question; and as soon as the details of the new method had been worked out, we began our final determinations by taking, according to the old method, the tare of the balloon above described when empty, so as to obtain a definite standard of comparison for further results.

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[1] Published by the Smithsonian Institution, Washington.

We, however, varied the method of Regnault in so far that we always filled the globe with hydrogen before exhausting the interior. As with this exceedingly light material the weight of the residual gas seldom exceeded one half a milligram, an error as great as one fifth in the capacity of the balloon or in the tension of the residual gas would cause no appreciable difference in the value of the small weight we sought to estimate. The details of a single example will be sufficient to illustrate the procedure.

Determination No. 1.

A current of hydrogen gas from the electrolytic generator described in our previous paper[1] was run through the balloon from Saturday, May 25th, at 4 o'clock P.M., to Monday, May 29th, at 10 o'clock A.M., 1889, the balloon standing in calorimeter case connected with larger balloon to receive overflow. At moment of closing, the height of barometer and temperature of the case were observed, but these data are not required for the present determination, and will be given hereafter when used for calculating the specific gravity of hydrogen. The balloon was exhausted with an excellent mechanical air-pump,[2] and the tension of the residual gas measured by means of a siphon manometer interposed between the balloon and the pump. The form of manometer used is shown by Figure 2. It was made in the laboratory, and in filling it with mercury the liquid metal, purified by repeated distillation, was boiled in the tube with the greatest care. For convenience, the difference of level of the mercury in the two arms was measured with a cathetometer constructed by the Société Genevoise, but it might have been estimated with sufficient accuracy by the millimeter scale of the instrument. Tension in balloon after exhaustion $456.95 - 455.55 = 1.40$ mm.

Assuming 0.4164 as the approximate value of the weight of hydrogen gas filling the balloon at 763.10 mm. and 21°.08 C. (p. 535), the weight of the residual gas at 1.4 mm. and same temperature would be 0.00076 gram or 0.76 mg. No exact observation of the temperature of the balloon was necessary; for a difference of 4° C. would not alter the above value more than $\frac{1}{100}$ mg. and we may therefore assume that the temperature of the balloon was the same as that of the laboratory, which at the time was 21° C. The correction for lessened buoyancy (increased weight) on account of the contraction of the balloon by atmospheric pressure amounts, as has been shown, to 1.98 mg.,[1] and this added to 0.76 makes the total correction 2.74 mg. When the balloon was hung on the balance, the weight required to complete the tare was 2.5600 grams. Hence we have:

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[1] This Journal **10**, 102 (1888); and Proceedings Am. Acad. **23**, 168 (1888).

[2] Author's Chemical Physics, p. 331.

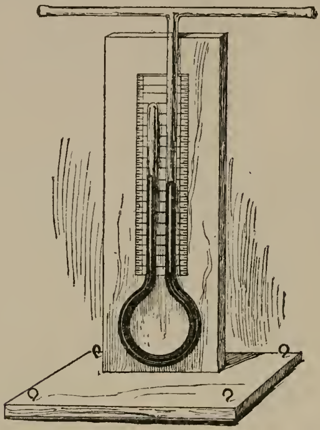

Fig. 2.

Weight of balloon exhausted, ...		2.5600 grams.
Correction for residual gas, . .	0.76 mg.	
" " lessened buoyancy,	1.98 "	27 "
Tare of empty balloon, ...		2.5573 "

Two other determinations were made in the same way, and the three results are united in the following table.

Summary.

Tare of empty balloon, 1st value, . . .	2.5573 grams.
" " " 2d " . . .	2.5572 "
" " " 3d " . . .	2.5574 "
Mean value, ...	2.5573 "

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[1] This Journal **10**, 194 (1888); and Proceedings Am. Acad. **23**, 184 (1888).

Tare of the Empty Balloon by Chemical Method.

The general theory of this method has already been stated. The balloon is filled with carbonic acid gas by displacement, and the tare taken. The gas is then drawn through a series of absorption tubes, as in the process of organic analysis, and the sum of the increased weights of these tubes gives the weight of the total contents of the balloon at the time the tare was taken. The weight of the balloon filled with carbonic acid gas less the weight of the carbonic acid thus determined is obviously the tare of the empty balloon required. In attempting to perfect this apparently simple experimental method we met with unexpected difficulties, arising from several circumstances.

In the first place, in order to wash out from the balloon the last traces of carbonic acid, it was necessary to draw through the apparatus a very large volume of air, and the system of purifiers and desiccators needed absolutely to free the atmospheric air from the least admixture of carbonic acid or aqueous vapor was found to be far more extensive than we anticipated. In the second place, since the globe held, at the ordinary temperature of the laboratory and at the average pressure of the atmosphere, no less than nine grams of gas, the common potash bulbs used in organic analysis were wholly inadequate for our requirements, and we only succeeded after many trials in finding a form of apparatus by which so great an amount of carbonic acid could be determined with the necessary accuracy, that is, within a few tenths of a milligram. The arrangement finally adopted is shown in Plate III. The balloon is represented standing in its covered metallic case, in which it is placed the moment it is taken from the balance. On the right of the balloon and below it is a system of tubes for purifying and drying the atmospheric air which enters from outside the laboratory by the flexible tube on the extreme right. On the left of the globe is a system of tubes for absorbing the carbonic acid. The flexible tube on the left is connected with a Bunsen pump through a form of Mariotte's flask,[1] and by this means a current is maintained through the whole system, under constant pressure.

Purifying and Drying Apparatus.

The air entering as we have described, passed first through a wash-bottle of familiar construction, containing a solution of potassic hydrate, sp. gr. = 1.44, and then through a similar wash-bottle containing a concentrated solution of baric hydrate; and if the rapidity of the current was not greater than two bubbles a second, this double washing was found sufficient to remove the last traces of carbonic acid. Indeed, as soon as the baryta water showed the least indications of cloudiness, the solutions were renewed. It was not so easy to remove the last traces of moisture.

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[1] This Journal **10**, 96 (1888); and Proceedings Am. Acad. **23**, 163 (1888).

After the air had passed the washing flasks it entered a system of desiccators, shown in the lower half of the plate, where in small bubbles it travelled up first one tube, and then a second tube, both 5½ feet long, and filled with concentrated sulphuric acid previously boiled with a small amount of ammonic sulphate to remove all nitrous fumes. Leaving the second of these tubes it entered an elongated bulb four inches long by two inches in diameter filled with phosphoric anhydride; and the fact that prolonged contact with sulphuric acid is not sufficient to remove the last traces of moisture, was shown by the circumstance that after the current has passed for several days the dry white powder at the opening of the bulb showed signs of deliquescence.

Our phosphoric anhydride was prepared by burning common yellow phosphorus in a large sheet-iron drum, through which a current of dry air was drawn with sufficient rapidity to maintain the phosphorus in rapid combustion, and the bottom of the drum was made tunnel-shaped so that the anhydride could be shaken down into a self-sealing fruit jar as fast as it formed. As thus prepared the anhydride has a slight odor, which it loses after a prolonged current of dry air has been drawn through the powder; and after our drying tubes had been filled, their contents were submitted to a preliminary treatment of this sort, and not until long after all perceptible odor had disappeared were they used in our work. We noticed that after the anhydride had been used for some time it appeared more granular and lost in part its hygroscopic power. In order to make sure of this point, the apparatus as far as described having been in use for several weeks, we connected with the first phosphoric anhydride tube a weighed tube containing fresh anhydride. After drawing air through the system at the same rate and during the same time as in a carbonic acid determination, we reweighed this second tube and found that it had gained 5.5 mg. We next added to our system the U tube filled with phosphoric anhydride, which is shown in Plate III immediately before the balloon, and repeated the experiment. There was then no gain in weight perceptible. The observations were as follows:

Before interposing the U *Tube.*

		H.	T°.	R.
1st weight P_2O_5 tube,	25.9212 grams.	295.7	20.0	302.7
2d " "	25.9267 "	295.2	20.8	301.4
	0.0055 "			1.4

After interposing the U *Tube.*

		H.	T°.	R.
1st weight P_2O_5 tube,	25.9268 grams.	299.3	19.6	306.7
2d " "	25.9268 "	299.2	21.6	304.6
				2.1

In this table the column headed H contains the barometric pressure at time of weighing in tenths of an inch; that headed T° gives the corresponding temperatures of the balance case in centigrade degrees. By adding to the values H the quantities $(27-T)°$ we obtain the values R, and these are the barometric heights which would give an atmosphere of the same density, and therefore exerting the same buoyancy, as the atmosphere at the time of weighing if the temperature were uniformly 27° C. The correction that should be made for differences of temperature and pressure at successive weighings can at once be calculated from these values. We found by experiment that for the phosphoric anhydride tube used in these and in subsequent determinations, the correction amounted to 0.04 mg. for each tenth of an inch change of pressure, and hence in the above weighings the correction is too small to be appreciable. This simple method of correcting weights for changes in the buoyancy of the atmosphere has been described in a previous paper.[1] In order to apply it readily, the barometric heights, although usually read in millimeters, were often also noted, as here, in tenths of inches, and the instrument we used was provided with both scales.

It is obvious from the above experiments that the hygroscopic power of phosphoric anhydride becomes impaired before the powder actually deliquesces, and we have dwelt on the point because the experience was of great importance in our investigation by leading us to add the second anhydride tube to our system, and also to watch carefully the condition of its contents, and to replace the tube as soon as the least change was perceptible. We attribute the change to a glazing of the amorphous grains due to the forming of a coating of glacial phosphoric acid, but the effect is one that would not be noticed except under such extreme conditions as existed in our work. We now pass to the system of absorption tubes on the other side of the balloon.

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[1] Proceedings Am. Acad. **18**, 55.

Absorption Apparatus.

The apparatus for the absorption of the carbonic acid gas must meet very opposite requisitions. In the first place, it must offer a sufficiently large mass of absorbent to the pure gas which first comes to prevent overheating from the rapid chemical combination. In the next place, it must be capable of removing the last traces of carbonic acid from the air which is afterwards drawn through the tubes. Lastly, it must not be so heavy or so complicated that it cannot be promptly and sharply weighed, and the correction for changes of temperature and pressure between successive weighings accurately estimated.

After trying in various ways to enlarge and modify the different forms of potash bulbs and spiral tubes in general use (and in these attempts we had the aid of a skilful glassblower), we found that we could reach a more accurate result with a system of separate tubes, in spite of the number of weighings they involved. To absorb the great mass of the carbonic acid we used the simplest form of gas-washer, shown in Plate III, at *A*. The bulb had a capacity of 200 cc., and in this we placed 75 cc. of a solution of potassic hydrate having sp. gr. = 1.443. When empty the bulb weighed only 57 grams, and when filled about 165 grams. Assuming that the potash was fully neutralised, less than one half of this amount would be sufficient to combine with nine grams of carbonic acid; but to insure prompt action and avoid excessive heating the amount given is required.

The potash tube was followed by a small U tube, four inches long, with ground caps filled with finely granulated soda lime, and weighing when full about 40 grams. (See *B*, Plate III.) To this was united a similar U tube containing phosphoric anhydride to hold the aqueous vapor, which is brought over by the gas current in no inconsiderable amount from the potash solution and the soda lime, in consequence of the heat set free by the absorption. The anhydride tube weighed when full about 25 grams, and is shown at *C*. Next was a third U tube filled with glass beads and having a few drops of strong sulphuric acid at the bend. This tube, *D*, was not weighed, but was necessary in order to indicate any sucking back of the air and to prevent any vapor from thus reaching the phosphoric anhydride. The double bulb forming the end of the system, shown at *E*, was made by melting together the usual inlet tubes of two gas-washers like *A*. In this we placed 50 cc. of a standard solution of baric hydrate, and the peculiar construction was necessary in order to provide against regurgitation in consequence of back pressure. The solution is easily washed out of the bulbs, and when retitrated at the end of the process gives the amount of carbonic acid, if any, which escaped the other absorbents. All of these tubes were united into one system by rubber connections carefully lubricated both inside and out with vaseline, a soft paraffine which had previously been melted and heated to remove every trace of moisture.

The manipulation of this apparatus was an interesting experiment. When all had been set up as shown in Plate III, the globe being full of carbonic acid, the Bunsen pump was first started, and after a constant suction (regulated by the Mariotte's flask before described) had been established, we cautiously opened the cock of the balloon, which connected with the potash bulb, closely watching the flow of gas. As soon as this flow began to slacken, we as cautiously opened the farther cock, by which air was admitted to the balloon through the line of purifiers, still closely watching and regulating the flow. We then noticed a striking phenomenon. As pure carbonic acid was now passing into the potash bulb, the air mixing but slowly with the heavy gas at the surface of contact as the level sunk in the balloon, the absorption at first was complete. If the air supply from behind was not sufficient, a partial vacuum formed in *A*, and air was drawn back through the tubes in front, as indicated at once by the bubbles at the bend of *D*; but if the supply was carefully regulated, a perfect equilibrium could be maintained in the tubes beyond, and we have seen the carbonic acid flow into the potash bulb for half an hour without more than a few bubbles of air passing through the sulphuric acid at the bend of *D* in either direction.

After a while, however, when the great mass of the carbonic acid has been absorbed, bubbles of air begin to pass through *D*, and also bubble through the baryta water beyond, and soon a steady current is established throughout the whole apparatus, which may then be left to take care of itself. If the current does not exceed in rapidity two bubbles a second, it may be allowed to flow for twenty-four hours without risk, and in that time every trace of carbonic acid will have been washed out of the balloon. The suction should now be stopped, and the cocks of the balloon closed. The tubes *A*, *B*, and *C* may then be disconnected, and after they have come to equilibrium in the balance case reweighed. The double bulb *E* must also be disconnected, the baryta washed out into a suitable bottle, and the solution retitrated with oxalic acid.

As the weights of the tubes *A*, *B*, and *C* must be corrected for the buoyancy of the air, it is essential to note the temperature of the balance case and the height of the barometer at the time of each weighing. The corrections in question may be considered under two heads; first, that made necessary by a change of temperature or pressure between successive weighings; secondly, that required to eliminate the effect of atmospheric buoyancy on the total weight of carbonic acid absorbed.

The first correction is best made by the method already described, and the application of this method was greatly facilitated in the present investigation by the circumstance that the same tubes, with the same weights of contents, were used in all the carbonic acid determinations made. We were able to determine once for all for each tube the correction required for a variation of one tenth of an inch in the barometric height reduced to 27° C.,[1] and the correction in any case could be found by a simple multiplication. Thus we estimated that the correction for one tenth of an inch in the barometric height reduced to 27° C. was:

For the potash bulb before absorption, . .	0.306	milligram.
" " " after " . .	0.321	"
" soda lime tube, ...	0.067	"
" phosphoric anhydride tube, . . .	0.040	"

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[1] That is, reduced to the height which would be required to give at the temperature of 27°, an atmosphere of the same density and buoyancy as that at the temperature of the balance case when the tube was weighed. See Proceedings Amer. Acad. **19**, 55.

Calculation of Correction for Potash Bulb.

	Before Absorption.	After Absorption.
Weight of glass, ...	57.45 grams.	57.45 grams.
Volume of glass = 57.45 ÷ 2.5, .	23 cc.	23 cc.
" KOH solution, . . .	75 "	80 "
	98	103
" brass weights, 164 ÷ 8.2,	20 "	
" " " 173 ÷ 8.2,		21 "
Uncompensated volume, ...	78 "	82 "
Air displaced at 27° C. and 300 tenths of an inch.		
1.176 × 78	91.928 mg.	
1.176 × 82		96.332 mg.
Variation for $\frac{1}{300}$, ...	0.306 "	0.321 "

The correction of the total weight of carbonic acid for the buoyancy of the atmosphere was not so simple a problem; but by using the same bulb and nearly the same volume of the same solution of potassic hydrate in every case, it was sensibly the same for all the determinations. The specific gravity of the solution of potassic hydrate before the absorption was 1.443, and tested in two separate determinations after absorption it was found to be 1.464 in each case. Using now the arithmetical means of the weights of the potash bulb in the three determinations under consideration, it was easy to find an average value for the correction thus:

Average weight of potash bulb before absorption,	165.02 grams.
Weight of glass, ...	57.45 "
" solution of KOH, ...	107.57 "
Volume of solution of KOH = 107.57 ÷ 1.443, .	74.55 cc.
Average weight of potash bulb after absorption, .	173.57 grams.
Weight of glass, ...	57.45 "
	116.12 "

Volume of solution of KOH = 116.12 ÷ 1.464,	79.32 cc.
Difference of volume = 79.32 — 74.55,	4.77 "
Weight of CO_2 absorbed in potash bulb = 173.57 — 165.02,	8.55 grams.
Volume of brass weights = 8.55 ÷ 8.2,	1.04 cc.
Uncompensated volume = 4.77 — 1.04,	3.73 "
Weights of 3.73 cc. of air at 300 tenths inch and 27° C. = 1.176 × 3.73 = corr. required,	4.39 mg.

In this calculation we have necessarily left out of the account both the small amount of carbonic acid absorbed by the soda lime and the water carried by the current from the potash bulb to the connecting tubes; for the increased weight of these tubes results from both these causes, whose relative effects or whose influence on the correction we cannot estimate. That they would tend to raise slightly the value of the correction is obvious; and if we assume, as we have in the following calculations, that the value is 4.5 milligrams, we shall approximate as nearly to the precise amount as circumstances will permit. For all these corrections the data are only known within certain narrow limits; but the total uncertainty thus arising does not exceed two or three tenths of a milligram in the final result.

In weighing the potash bulb and U tubes it is of course essential that they should be left in the balance case until a perfect equilibrium of temperature has been reached, and then they must be weighed when open so that a perfect equilibrium of pressure on the inside and outside of the glass may be secured. And since we were here aiming at very great accuracy, we felt it important to inquire further whether any gain of weight from hygroscopic moisture was possible during the time necessary to verify the weight while the tubes remained open on the scale pan. We therefore carefully investigated this point. The air in the balance case was kept as dry as possible by an open dish of sulphuric acid, and the experiments were made under such conditions. It was found that the weight both of the potash bulb and of the soda lime tube remained absolutely constant, hour and hour together, except so far as they were influenced by changes of temperature and pressure, but the weight of the phosphoric anhydride tube slowly but uniformly increased at the rate of 0.025 mg. per hour. We followed the change on one occasion from 10 h. 45 m. A. M. to 6 h. 15 m. P. M., and during these seven hours and a half the gain was 1.9 mg., while the changes of temperature and pressure meanwhile were not enough to cause a sensible difference in the atmospheric buoyancy. Such experiments were continued for a sufficient length of time to enable us to confirm the values of the corrections above given, and they gave us great confidence in our weights. They showed that the only precaution necessary for accuracy was to close the tubes as soon as they were disconnected, and to leave each of them closed in the balance case until it was time to take the weight. The U-shaped tubes with perforated ground stoppers, by which connection with the lateral tubes can be instantly opened or closed, are admirably adapted to this work. As an example, we give next the details of one determination of carbonic acid by the method we have described

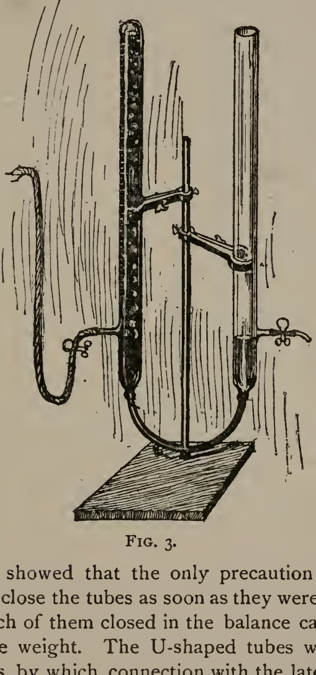

Fig. 3.

Details of a Determination of Carbonic Acid.

The gas was generated from statuary marble and dilute hydrochloric acid in an apparatus precisely similar to that described and figured by us in a previous paper.[1] It was first washed by a solution of potassic bicarbonate, and then, having passed in succession over calcic chloride, sulphuric acid, and phosphoric anhydride, it was conducted into the balloon and overflow in the manner already described. The gas was tested by leading the current from the overflow into a familiar form of nitrogen apparatus filled with a solution of potassic hydrate (Fig. 3), and not until no measurable residue was left by a full liter of gas was its condition regarded as satisfactory. The balloon stood in the calorimeter case, and when the cocks were closed with the precautions already described, the temperature of the case and the height of the barometer were observed, and although these values are not needed for determining the tare of the empty balloon, they will be used for determining the density of carbonic acid hereafter. The balloon was then disconnected and hung on the balance, and its tare found to be

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[1] This Journal **10**, 100 (1888); and Proceedings Am. Acad. **23**, 166 (1888).

$$W = 11.5907 \text{ grams.}$$

The balloon was then transferred to its metal case, and, having been mounted as shown in Plate III, the determination of the weight of its contents proceeded as just described.

Potash Bulb.

	Grams.	H.	T°.
1st weight of potash bulb,	165.3388	299.99	25.8
2d " " "	174.0132	299.83	27.0
	8.6744		
Correction[1] for change of H and T,	4		
	8.6740		

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[1] Since the volume and density of the potash solution used were closely the same in all the determinations, whether compared before or after the absorption, the value of the correction may be assumed to be the same in all cases, and, as has been shown at page 526, amounts to 0.306 mg. before absorption and 0.321 mg. after absorption for every change of one tenth of an inch pressure or 1° centigrade temperature from the standard of 300 tenths inch and 27° C. or 300° absolute temperature. The correct mode of calculating the correction in any case is to reduce both weights to what they would appear to be at H = 300 and $T_0° = 300 = 27°$ C. before taking their difference, using the value 0.306 for the smaller of the two, and 0.321 for the larger.

299 89 at 25.8° corresponds in buoyancy to 301.09 at 27°.
299.83 4t 27° " " " 299.83 "
301.09 — 300 = 1.09 and 1.09 × 0.306 = 0.33 addative.
299.83 — 300 = —0.17 and —0.17 × 0.321 = —0.05 subtractive.
Then 165.3388 + 0.33 = 165.33913
174.0132 — 0.05 = 174.01315
8.67402 as before.

As regards the sign of the correction, notice that, when reduced to H = 300, the buoyancy becomes less and the *apparent* weight greater if the previous pressure was above 300, and *vice versa*.

Soda Lime Tube.

	Grams.	H.	T°.
1st weight of soda lime tube,	42.8731	299.54	26.6
2d " " " "	43.1857	299.87	27.4
Correction insensible,	0.3126		

Phosphoric Anhydride Tube.

	Grams.	H.	T°.
1st weight of anhydride tube,	39.5196	299.50	27.0
2d " " " "	39.5493	300.00	27.2
Correction insensible,	0.0297		

Standard Solution of Baric Hydrate.

Before absorption, 50 cc. required 46.60 cc. solution of oxalic acid.
After " " " 43.65 " " " "

2.95

One cc. of decinormal solution of oxalic acid contains 0.0126 gram of $H_2C_2O_4.2H_2O$, corresponding to 0.0044 gram of CO_2.

$$2.95 \times 0.0044 = 0.0130 \text{ gram of } CO_2.$$

Total Weight of Carbonic Acid.

	Grams.
From potash bulb,	8.6740
" soda lime tube,	0.3126
" anhydride tube,	0.0297
" titration,	0.0130
	9.0293
Reduction to vacuum,	45
	9.0338
Tare of balloon and gas,	11.5907
Tare of empty balloon,	2.5569
Value by Regnault's method,	2.5573

The value of the tare of the empty balloon found by the new chemical method is directly comparable with that obtained by the Regnault method, since there was no change in the balloon meanwhile. But after this determination was finished, the balloon, as it remained standing in its case, having been exposed to the direct sunshine of an unusually hot June day, some of the cerate lubricating the stop-cocks melted and ran down into the tubulatures below, from which it had to be removed. Thus the tare was lessened by nearly a centigram. It was easy, however, to determine the exact loss, and as in a like investigation, even when using the greatest care, one must ever be liable to accidents of this sort, it is important to dwell on this point.

In losing the tare we had apparently lost the thread of our investigation, but we were readily able to recover this thread without interrupting the general course of the work. It must be borne in mind that our immediate object was to obtain by the chemical method a series of results for the tare of the empty globe which could be compared with the mean value 2.5573 obtained by the method of Regnault. Here had come a change of tare, and we could obviously find a new standard of comparison by redetermining the new value by the old method. But this was not necessary. In the first determination by the chemical method, we had observed with great precision the pressure and temperature at which the balloon was filled. We do the same in the second determination, to which we next proceed, although these values are not needed in this determination, by itself considered, any more than they were in the first. If now from the tare of balloon and gas in the first determination (11.5907) we deduct 2.5573, we have the weight of carbonic acid which the balloon contains at a known temperature and pressure as found by the method of Regnault. If we deduct the same quantity from the tare found in the second determination, we have the weight of gas which the balloon holds at another temperature and pressure by the same method. If now there has been no change of tare, these two weights ought to agree exactly when one is reduced to what it would have been under the conditions at which the other was taken; and if there has been a change of tare, the difference of the weights thus reduced will give the exact amount of the loss, on the basis solely, let it be noticed, of results obtained after the method of Regnault. Thus we have:

			Grams.
By No. 1, weight of CO_2 at	763.85 mm. and	25.08°	9.0273
" No. 2, " "	756.73 " "	22.40°	9.0334
Weight No. 1 reduced at	" "	" "	9.0241
Loss of tare,			9.3 mg.

Obviously the accuracy of this result depends upon the accuracy with which the observations of temperature and pressure were made, and upon the correctness of the data on which the reductions are based. That the accuracy is extreme will appear from a comparison of the values of the specific gravity of carbonic acid, given on page 537, which were deduced from the same elements. And although in such work as this there is an obvious liability to error from just such a change of tare as we have been discussing, yet the loss or gain thus resulting is usually of such a magnitude that it cannot be overlooked.

Besides the one of which the details have been given, we made by the chemical method two other determinations of the tare of the empty globe in precisely the same manner as before described, and obtained the values 2.5481 and 2.5475 respectively. In order to bring these results into comparison with that obtained by the first determination, or those obtained by the method of Regnault, we must add 9.3 mg. to each value. We then have for

Tare of Empty Balloon.

	Regnault's Method.	Chemical Method.
No. 1,	2.5573	2.5569
No. 2,	2.5572	2.5574
No. 3,	2.5574	2.5568
Average,	2.55730	2.55703

These results are essentially identical, and the two methods confirm each other. But having reached this important conclusion, which was the main object of our investigation, we freely concede the preference to Regnault's method. The difference between the results of the two methods, as here exhibited, is insignificant; but so long as the validity and value of the correction for the contraction of the balloon on exhaustion has been thus established, Regnault's method will be preferred, because it is practically more simple, and hence the results are more accordant than those obtained by the chemical method first described in this paper.

During the course of our investigation there were two marked changes in the tare of our balloon. One of these has been described. The other arose from the circumstance that the thin paraffine (vaseline) which was most suitable for lubricating the stop-cocks during the winter, no longer kept the joints tight when the heat of approaching summer rendered the material more liquid; and it became necessary to remove the stoppers and relubricate them, and it was the excess of cerate then used which melted and ran into the tubulatures subsequently.

There are then three separate values of the tare of the empty balloon to be used in our further calculations, all determined by or dependent upon Regnault's method, and all known with equal accuracy. These values we shall distinguish by the letters A, B and C, and we shall designate by the same letters the experimental data or calculated results into which these values enter as elements.

Tare of Empty Balloon.

Values.	
A	2.5098 grams.
B	2.5573 "
C	2.5480 "

Density of Air freed from Moisture and Carbonic Acid.

In these determinations the balloon was placed in the calorimeter case and connected with the Bunsen pump through an overflow jar. Air was then drawn into it through the purifiers we have described, and the reflux current which followed for a moment when the inlet cock was closed was supplied from the previous overflow. In other respects the determinations were made as before described, and we obtained the following data for the weight of air held in the balloon at different temperatures and pressures.

Summary of Air Weights.

A No. 1, weight of air at 762.63 mm. and 18°.52 = 6.0347 grams.
A " 2, " " 758.71 " " 19°.96 = 5.9745 "
B " 1, " " 750.30 " " 23°.32 = 5.8411 "

Reducing now these weights to what they would have been at the temperatures and pressures we have assumed as standards, we obtain the following comparable values:

Reduced Air Weights for

H = 761.99 mm. = 300 d. in.[1] and
T = 27° C. = 300° absolute temperature.

A No. 1	5.8584 grams.
A " 2	5.8588 "
B " 1	5.8586 "
Average value,	5.8586 grams.[2]

Density of Hydrogen.

We have for the weight of hydrogen held by the balloon the following data:

B No. 1, weight hydrogen at 763.10 mm. and 21°.08 = 0.4164 gram.
B " 2, " " " 764.92 " " 20°.52 = 0.4178 "
B " 3, " " " 758.96 " " 22°.75 = 0.4123 "

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[1] We shall use the abbreviation d. in. for tenths of an inch, after the analogy of d. m. for tenths of a meter.

[2] In the calculations of density and specific gravity, a still further, although wholly unimportant, correction has been made for the buoyancy of the air on the *brass* weights used to complete the tare in weighing the balloon, and in this connection it must be borne in mind that the *platinum* or *aluminum* fractions of a gram in a set of weights have always been adjusted to the larger *brass* weights in the air, and are therefore the equivalent of *brass* weights of the same denominations. The volume of the counterpoise was adjusted when the balloon was full of air; but although the compensation may be perfect through all ordinary changes of temperature and pressure, it cannot be regarded as absolute. In a laboratory, such changes seldom amount in the aggregate to more than the equivalent of one twentieth of the normal atmospheric pressure; and although such a variation might not produce a sensible effect on the apparent weight of the small amount of brass used in our weighings, twenty times this effect, which we should have if the brass weights were wholly uncompensated, might be an appreciable quantity. In weighing the balloon the largest amount of brass weights used was about 11.5 grams, which at 300 d. in. and 27° C. displace 1.6 mg. of air. One twentieth of this value would be barely, if at all, perceptible, but the whole quantity might cause a serious error in our results.

The tare of the empty balloon as first found by Regnault's method was 2.5573 grams; and we must assume that in the system consisting of balloon counterpoise and weights there may be outstanding a very small uncompensated volume, so that the true tare would be represented by

$$W_R = 2.5573 \pm w.$$

We next find the weight of the balloon filled with hydrogen gas, and it is obvious that under standard conditions the true weight, or

$$W' = 2.5573 \pm w + 0.4076 - w',$$

where w′ represents the buoyancy of air on 0.4076 gram of brass. So the true weight of the balloon filled with air must be

$$W'' = 2.5573 \pm w + 5.8594 - w'',$$

Reduced Weights.

H = 300 d. in. T = 27° C.

B No. 1,	0.4076
B No. 2,	0.4072
B No. 3,	0.4081
Average,	0.4076

Specific Gravity of Hydrogen.

Air = 1.

The values were obtained by dividing each of the weights of hydrogen above given by the average weight of air (5.8586), after reduction for the temperatures and pressures at which the hydrogen weights were observed. The calculations were verified by dividing each of the reduced weights of hydrogen by the average reduced weight of air as above, and the same figures were obtained in both ways.

B No. 1, ...	0.06957
B No. 2, ...	0.06951
B No. 3, ...	0.06966
Average, ...	0.06958
Average, using values of tare by chemical method,	0.06962

where w'' represents the buoyancy of air on 5.8594 grams of brass. In like manner, the true weight of the balloon filled with carbonic acid gas is

$$W''' = 2.5573 \pm w + 8.9564 - w''',$$

where w''' is the buoyancy of air on 8.9564 grams of brass.

Taking 1.176 mg. as the weight of 1 cc. of air at 300 d. in. and 27° C., the standard conditions to which the weights have been reduced, we have

$$w' = 0.05 \text{ mg.}, \qquad w'' = 0.84 \text{ mg.}, \qquad w''' = 1.28 \text{ mg.};$$

and further,

$W' - W_R = 0.4076 - 0.00005$ gram. True weight of hydrogen.
$W'' - W_R = 5.8594 - 0.00084$ " " " " air.
$W''' - W_R = 8.9564 - 0.00128$ " " " " carbonic acid.

These corrections should be applied to the weights before calculating the specific gravities, although they only alter the last values one or two units in the last decimal place; and in this paper, as is usual, the decimals are carried out one figure beyond the limits of accuracy.

In the chemical method we also took the weight of the balloon filled with carbonic acid gas, and, as before, we have

$$W''' = 2.5573 \pm w + 8.9564 - w'''.$$

Then by chemical means we determined the absolute weight (*in vacuo*) of the carbonic acid which the vessel held, that is, the quantity represented by $8.9564 - w'''$. Subtracting this value from the total weight, we obtained the tare of the empty balloon by the chemical method, and this obviously is

$$W_C = 2.5573 \pm w.$$

Thus, the buoyancy of the air on the weights is eliminated, and W_C is directly comparable in all its relations with W_R.

Specific Gravity of Oxygen.

Hydrogen = 1.

In this investigation we have not made an additional determination of the specific gravity of oxygen gas referred to air, for the causes of error which are serious in the case of hydrogen are not appreciable when working with the heavier gas, and we cannot expect to improve on the results of Regnault. Assuming, then, for the specific gravity of oxygen gas referred to air the value 1.10562, as obtained by Regnault and corrected by Crafts, and dividing this value by each of the values for the specific gravity of hydrogen gas given above, we have the following values for the specific gravity of oxygen referred to hydrogen:

B No. 1,	15.892
B No. 2,	15.907
B No. 3,	15.873
Average,	15.891
Average of chemical method,	15.882
Value found by Lord Rayleigh,	15.884

Density of Carbonic Acid.

For the weight of carbonic acid gas held in the balloon at different temperatures and pressures we have the following data:

B No. 1,	weight of CO_2 at	756.73 mm.	and 22°.40	9.0334 grams.
C No. 1,	" "	760.50 "	" 25°.56	8.9821 "
C No. 2,	" "	759.13 "	" 26°.60	8.9348 "

Taking now the average value of the weight of air held in the balloon at 300 d. in. = 761.99 mm. and 27° (viz. 5.8586 grams), and reducing this weight to what it would have been under the condition at which each of the four weights just given was observed, and then dividing each of these weights (corrected as by previous note) by the weight of air under the same conditions, we obtain the following results:

Specific Gravity of Carbonic Acid. Air = 1.

	Wt. of CO_2.	Wt. of Air.	H.	T.	Sp. Gr.
B No. 1,	9.0321	5.9088	756.73	22°.40	1.52858
C No. 1,	8.9808	5.8753	760.50	25°.56	1.52855
C No. 2,	8.9335	5.8445	759.13	26°.60	1.52855
Average value,					1.52856
Average value by chemical process,					1.52854

Taking lastly the average value of the weight of hydrogen held in the balloon at 761.99 mm. and 27° (viz. 0.4076 gram), and dividing the several weights of carbonic acid by this weight reduced to the same conditions, we have,—

Specific Gravity of Carbonic Acid. Hydrogen = 1.

	Wt. of CO_2.	Wt. of H_2.	H.	T.	Sp. Gr.
B No. 1,	9.0321	0.4111	756.73	22°.40	21.971
C No. 1,	8.9808	0.4088	760.50	25°.56	21.971
C No. 2,	8.9335	0.4066	759.13	26°.60	21.971
	Average value, ...				21.971
	Average value by chemical process, .				21.957

The close agreement, indeed the essential identity, of these results should be noticed, as this fully substantiates the extreme accuracy of the method of recovering the lost tare of the empty balloon described on page 532. It is true that, as the values of the specific gravity of carbonic acid have been calculated with an average value of the several reduced weights of hydrogen or air, an error in these data would not affect the results; but any error in the observed weights of carbonic acid would appear to its full extent.

Moreover, the striking fact should not be overlooked that the specific gravity of carbonic acid gas referred to hydrogen approaches much more nearly 22, the half molecular weight of carbonic acid gas as generally assumed, than does that of oxygen gas when referred to the same standard, the corresponding whole number 16, and the significance of the circumstance is obvious. If we assume that the atomic weight of oxygen, as determined by Dr. Richards under my direction, is 15.87,[1] then the corresponding atomic weight of carbon would be 11.90, and the half molecular weight of carbonic acid 21.82. Theoretically, this number ought also to define the specific gravity of carbonic acid gas referred to hydrogen gas, if the two gases were compared under the same conditions of high temperature and indefinite expansion. But under the great pressure of our atmosphere the molecular volume of carbonic acid gas is known to be condensed to a measurably greater degree than the potentially equal molecular volume of hydrogen gas, and the result must be a proportionally increased density; and, moreover, the inequality in the condensation of the two gases must be increased by the circumstance that at the ordinary temperature of the air carbonic acid gas is below the critical point, while hydrogen gas is very far above it. If, however, this is true in the case of carbonic acid gas, our knowledge of the deviations from Mariotte's law compels us to infer that the same must be true in some small measure, although in a much less degree, in the case of oxygen gas; and it would lead us to expect that the specific gravity of oxygen gas referred to hydrogen gas would be slightly greater, certainly not less, than the corresponding half molecular weight. Now we have from the results published in this and our preceding paper:

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[1] This Journal **10**, 194 (1888); and Proceedings Am. Acad. **23**, 185 (1888).

Half molecular weight of carbonic acid gas, ...	21.82
Sp. gr. of carbonic acid gas (referred to hydrogen gas),	21.96
Half molecular or atomic weight of oxygen gas, . .	15.87
Sp. gr. of oxygen gas (referred to hydrogen gas), . .	15.88

It has been thought to discredit the low value of the atomic weight of oxygen we have found by the very easy but wholly gratuitous assumption that the hydrogen gas on which we experimented was impure, and we had intended in this investigation to demonstrate the identity of the gas from the several sources employed by a comparison of their specific gravities. We are under great obligations to Lord Rayleigh, who has relieved us from this necessity by anticipating the work. He has experimented on hydrogen gas, not only from all the sources we used, but also on gas which had been occluded by palladium, and has obtained the same result in all cases; namely, the value 15.884,[1] essentially identical with that which we have found in this investigation with the hydrogen gas from our electrolytic apparatus.[2]

This point, however, had not been overlooked in the previous paper. It was there shown that the results obtained, in *three distinct series of experiments*, with hydrogen gas prepared by *three different processes* and with *three different forms of apparatus*, were essentially identical.[3] On the doctrine of chances, such an agreement would have been practically impossible had there been an appreciable amount of accidental impurities in the gas from either of the sources. We say accidental impurities, for there may be inherent impurities common to the gas from all sources, of which we as yet know nothing; and, as we wrote before, "The question still remains, Is the hydrogen gas thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined."[1]

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[1] Proceedings of the Royal Society **45**, 425.

[2] This Journal **10**, 102 (1888); and Proceedings Am. Acad. **23**, 168 (1888).

[3] See table, this Journal **10**, 107 (1888); and Proceedings Am. Acad. **23**, 173 (1888).

It is not to be expected that our results, or those of our contemporaries, are final. The most that has been accomplished by recent investigation is to show that the ratio of the atomic weight of oxygen to that of hydrogen, deduced from the elementary substances, as we know them in their purest condition, is decidedly less than that of 16 to 1. The evidence as to the exact value of this ratio is still conflicting, and although after our experience we cannot see how greater accuracy could be gained by any variation of our process, we are far from claiming that our results have not been vitiated by unknown constant errors. Fortunately, an exact knowledge of the ratio is at present of no practical importance in chemical analysis. The only question on which the actual small indefiniteness has a bearing is the unit of atomic weights, a question that has been much discussed of late; but here, as it seems to us, one consideration should be conclusive.

Every one who has worked on the oxygen and hydrogen ratio knows that the resources of experimental science have been taxed to the utmost in these investigations. Greater accuracy is not to be expected with our present appliances, and yet there is an outstanding uncertainty amounting to more than one-half of one per cent. of the value. This corresponds to a variation of more than one unit in many of the higher atomic weights; and unless we are willing that these *chemical constants* should fluctuate to this extent with every new determination of the fundamental ratio, we must seek a more invariable basis. The most natural and stable unit is the atomic weight of oxygen, not only on account of the wonderful combining power of this element, but also because the ratio of the combining weights of most of the elements to that of oxygen are known with great precision; and many cogent reasons could be

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[1] This Journal **10**, 108 (1888); and Proceedings Am. Acad. **23**, 174 (1888).

PLATE I.

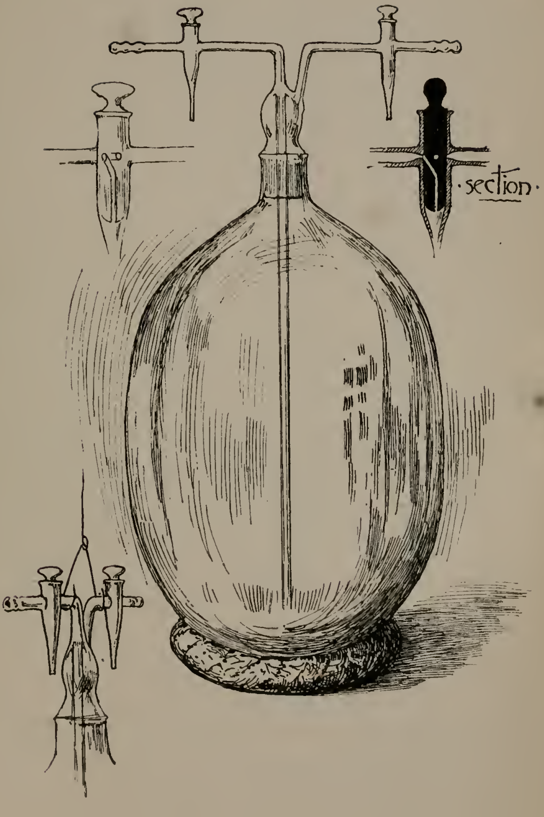


PLATE II.

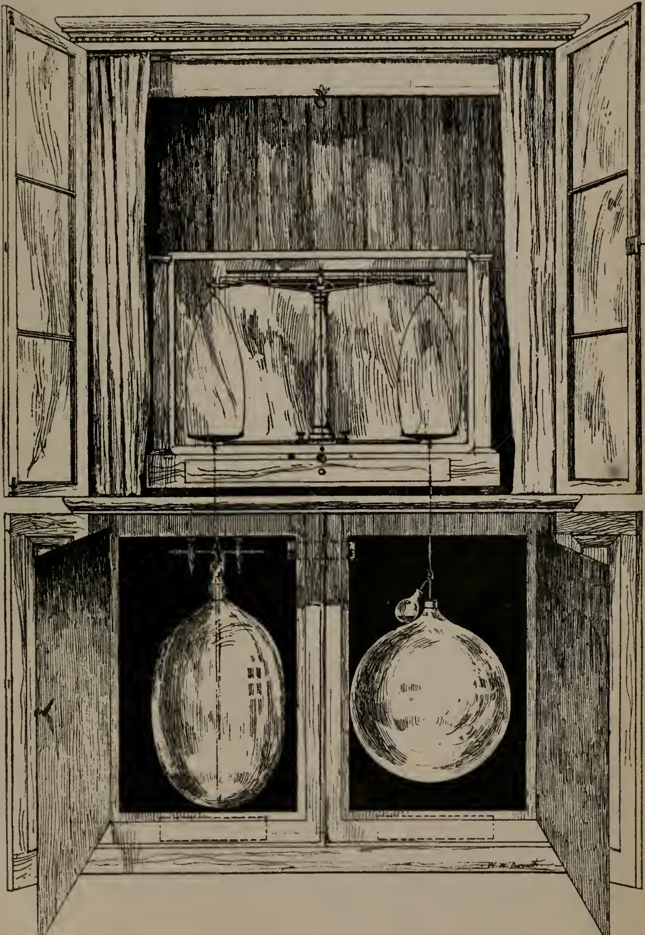
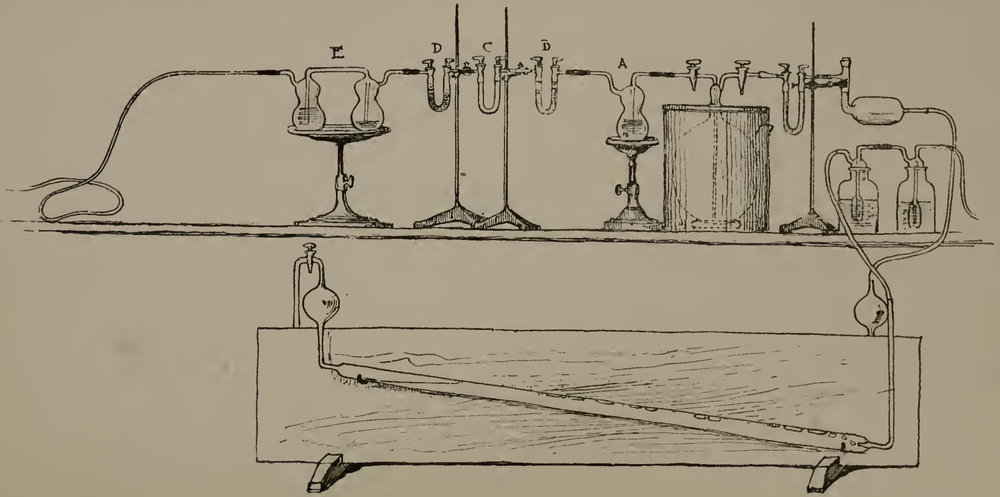


PLATE III.



urged for returning to the system of Berzelius, which referred all the other weights to that of oxygen, assumed to be 100. But this system would not exhibit to advantage the numerical ratios on which modern chemical classification is based. Hence for a provisional system we most warmly approve of that which assumes O = 16 as its basis, and of the best known atomic weights leaves only the value of H to vary with our changing knowledge. This system has all the stability it is possible at present to secure, and exhibits to advantage the relations which are important in classification. Moreover, it is no small recommendation to this system that a large number of the weights are whole numbers, within the limits of error of ordinary analytical work, and for this reason can be easily remembered.

In conclusion, I would express my obligations to my nephew, Dr. Oliver W. Huntington, for the great aid he has given throughout this investigation. With the help of his skill in glass-blowing I have been able to secure all the connections of my gas generators with melted or cement joints, except the direct connections with the globe, where india-rubber could not be avoided. He has also constantly assisted my impaired eyesight in the observations with barometer and thermometer on which the accuracy of the work greatly depended. I have likewise been indebted to Dr. Arthur M. Comey for making the titrations required, and to Mr. W. W. Bosworth for the drawings with which this paper is illustrated.

LXV.—ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

SECOND PAPER.

BY C. LORING JACKSON AND W. S. ROBINSON.[1]

In a previous paper[2] on this subject we were obliged to publish several results in an unfinished condition, because at the time we saw no chance of being able to continue the work together. Since then, however, unforeseen circumstances have allowed us to go on with the research, and in this paper we describe work which fills up most of the gaps in our former publication.

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[1] From the Proceedings of the American Academy of Arts and Sciences, communicated by the authors.

[2] This Journal **11**, 93 (1889).

The most important results contained in this paper may be stated briefly as follows. The reactions by which the bromdinitrophenylmalonic ester is formed have been made out to be the following:

$$\begin{aligned}
\text{I. } & C_6HBr_3(NO_2)_2 + CHNa(COOC_2H_5)_2 = \\
& NaBr + C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2. \\
\text{II. } & C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + CHNa(COOC_2H_6)_2 = \\
& C_6HBr_2(NO_2)_2CNa(COOC_2H_6)_2 + CH_2(COOC_2H_5)_2. \\
\text{III. } & C_6HBr_2(NO_2)_2CNa(COOC_2H_6)_2 + CH_2(COOC_2H_5)_2 = \\
& C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2. \\
\text{IV. } & CHNa(COOC_2H_6)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2. \\
\text{V. } & CHBr(COOC_2H_6)_2 + NaOH = NaBr + CHOH(COOC_2H_6)_2.
\end{aligned}$$

The proof of these reactions consisted in the isolation of tartronic acid from the mixture obtained by the saponification of the oily secondary product with hydrochloric acid.

The action of concentrated hydrochloric acid, or, better, sulphuric acid of specific gravity 1.44, upon the bromdinitrophenylmalonic ester has been studied, and we are able to correct some of the preliminary statements made on this subject in our first paper. The product is the bromdinitrophenylacetic acid

$$C_6H_2Br(NO_2)_2CH_2COOH,$$

which melts at 177°, and is formed, when hydrochloric acid is used, by the following reactions:

$$\begin{aligned}
& C_6H_2Br(NO_2)_2CH(COOC_2H_6)_2 + 2HCl = \\
& \quad 2C_2H_5Cl + C_6H_2Br(NO_2)_2CH(COOH)_2 = \\
& \quad 2C_2H_6Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COOH.
\end{aligned}$$

The crystalline silver salt of this acid was analysed, and proved to have the formula

$$C_6H_2Br(NO_2)_2CH_2COOAg \,.\, H_2O.$$

With sodic hydrate a deep Prussian green or with an excess a yellowish brown solution is formed, from which acids throw down a pale crimson precipitate, or a white one which becomes pale crimson when moistened with alcohol; none of these substances could be brought into a state fit for analysis, but we found that bromine was removed in their formation.

The bromdinitrophenylacetic acid is broken up when boiled with alcohol into bromdinitrotoluol and carbonic dioxide; boiling with water produces the same effect, but much more slowly. A few drops of sulphuric acid prevent the decomposition by boiling water. This conversion into bromdinitrotoluol gave us the means of determining the constitution of the bromdinitrophenylmalonic ester and its derivatives; as Messrs. W. B. Bentley and W. H. Warren have, at our request, worked out the constitution of the substituted toluol, and found that it is as follows:

$$CH_3 . Br . NO_2 . NO_2 . 1 . 3 . 4 . 6.$$

It follows, therefore, that all the substances mentioned in this and our former paper must have a similar constitution, and that in making the bromdinitrophenylmalonic ester from tribromdinitrobenzol the bromine atom replaced by the malonic radical is one of those which is at the same time para and ortho to the nitro groups, the one replaced by hydrogen is ortho to the two nitro groups, while the third atom of bromine, which remains unaltered, occupies exactly the same position as that replaced by the malonic ester radical—certainly a curious result.

Preparation of Bromdinitrophenylmalonic Ester.

Our longer experience in the preparation of bromdinitrophenylmalonic ester has led us to introduce several improvements into the process, which now we carry on as follows. A strong benzol solution of 20 grams of tribromdinitrobenzol (benzol is to be preferred to the ether used formerly, because the tribromdinitrobenzol is more soluble in it) is mixed with 16 grams of malonic ester, previously converted into sodium malonic ester by treatment with the sodic ethylate from 2.3 grams of sodium and about 100 to 125 cc. of alcohol, and the mixture allowed to stand over night at ordinary temperatures. The red solution thus obtained is treated with water, which separates it into two layers, a dark red aqueous solution containing the sodium salt of bromdinitrophenylmalonic ester and sodic bromide, and a benzol solution of the unaltered tribromdinitrobenzol with the oily product of the reaction. The two layers are separated with a drop-funnel, and the lower aqueous one acidified with dilute sulphuric acid; this throws down a yellowish white precipitate of the bromdinitrophenylmalonic ester, which is purified by crystallisation from hot alcohol, until it shows the constant melting point 76°.

In this way 20 grams of tribromdinitrobenzol gave 7.9 grams of the bromdinitrophenylmalonic ester,[1] and 5.1 grams of tribromdinitrobenzol were recovered from the benzol solution. Subtracting this from the 20 grams there are left 14.9 grams of tribromdinitrobenzol which entered into the reaction, and should have given the same weight, 14.9 grams of the product, so that the yield was 53 per cent. of the theory, or about the same as that obtained by the process as given in our first paper, which calculated in the same way becomes 50 per cent.

In the course of some other experiments the curious observation was made that it is not necessary to use sodic ethylate to bring about the action of malonic ester on the tribromdinitrobenzol, as a little of the red salt of bromdinitrophenylmalonic ester was formed when *aqueous* sodic hydrate was added to a mixture of the two organic substances. This recalls the observation of Victor Meyer,[2] that homologues can be obtained from benzyl cyanide by using the alkylhaloid with powdered solid sodic hydrate instead of sodic ethylate, or from desoxybenzoin by the use of an alcoholic solution of an alkaline hydrate.

Study of the Reactions by which the Bromdinitrophenylmalonic Ester is formed.

One of the most important points, which want of time prevented us from considering in our first paper, was the mechanism of the reactions by which the bromdinitrophenylmalonic ester was formed from the tribromdinitrobenzol, and accordingly this was one of the first points to which we turned our attention in taking up the subject again. The reaction consists essentially, as our analyses of the product showed, in the replacement of one of the bromine atoms in the tribromdinitrobenzol by the malonic ester radical $CH(COOC_2H_5)_2$, and of a second by hydrogen forming $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$, and the obscure part of it is the manner in which this second atom of bromine is replaced by hydrogen. The first step toward clearing up this obscurity was obviously to make out whether this atom of bromine was eliminated in the form of some organic compound, or as sodic bromide, which was done by the following quantitative determinations of the amount of sodic bromide formed in the reaction.

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[1] Dr. G. D. Moore, in his work with me on the action of sodium acetacetic ester on tribromdinitrobenzol, has found that a much better yield is obtained if the mixture is boiled for an hour under a return condenser. This observation was not made until the work described in this paper was finished and Mr. Robinson had left Cambridge, so that it was not convenient to try the experiment of boiling the solution of sodium malonic ester and tribromdinitrobenzol, nor did it seem very desirable to do so, as when we first took up the subject such an experiment was tried and seemed to yield very unfavorable results. I propose, however, to repeat the experiment next year, if I return to the study of these compounds. C. L. J.

[2] Ber. d. chem. Ges. **21**, 1291 (1888).

I. 20 grams of tribromdinitrobenzol were treated with the sodium malonic ester from 16 grams of malonic ester in the way already described, and, after precipitating the bromdinitrophenylmalonic ester from the aqueous solution with dilute nitric acid, and filtering it out, the amount of sodic bromide was determined by precipitation of argentic bromide from an aliquot part of the filtrate, and calculating the amount in the entire solution. In this way the whole solution was found to yield 13.81 grams of argentic bromide, corresponding to 5.88 grams of bromine. The benzol solution on evaporation yielded 5.1 grams of tribromdinitrobenzol, which had not taken part in the reaction, leaving 14.9 grams which had acted, and which would yield 5.89 grams of bromine, if two of the atoms of bromine had been removed from each molecule as sodic bromide.

II. 20 grams of tribromdinitrobenzol gave under the same conditions 13.8 grams of argentic bromide, corresponding to 5.87 grams of bromine, but only 4.9 grams of tribromdinitrobenzol were recovered unaltered. The 15.1 grams of tribromdinitrobenzol which entered into the reaction should have lost 5.96 grams of bromine.

Percentage of the theoretical amount of bromine removed from tribromdinitrobenzol in the form of sodic bromide:

I.	II.
99.86	98.49

These numbers agree as closely as could be expected, when the necessary sources of error in the process are considered, and prove that all the bromine removed by the reaction is converted into sodic bromide.

The second point to be determined was from what source the atom of hydrogen was obtained which replaced the atom of bromine. For this purpose we investigated the oily product of the reaction, and, after we had found that nothing definite could be obtained from it by distillation under ordinary pressures, or with steam, and that sodic hydrate or other alkaline saponifying agents gave most unpromising results, we tried heating it with strong hydrochloric acid in a sealed tube to 130° for 20 hours, as the bromdinitrophenylmalonic ester, which was dissolved in the oil, would be converted by this treatment into the corresponding phenylacetic acid, with the properties of which we were familiar, and which, therefore, we thought could be removed easily from the other products of the reaction. The tubes after heating contained an aqueous solution and a small amount of viscous matter, which gradually changed into an amorphous solid. These were separated by filtration, and the filtrate evaporated to dryness on the water-bath, leaving a crystalline residue, which was extracted with cold water to leave behind the bromdinitrophenylacetic acid present. The extract after being evaporated again on the water-bath gave crystals, which made up about one-half the amount of the residue from the first evaporation. They were freely soluble in water or alcohol, nearly insoluble in ether, and could be sublimed at temperatures below their melting point, forming glassy white thick needles or prisms, which melted at 185°. These properties proved that the crystals are tartronic acid, as they are identical with those given by Conrad and Bischoff for that substance.[1] We tried also to confirm this inference by an analysis, but the small amount of the acid which, after some unsuccessful experiments, remained at our disposal, little more than 0.1 gram, prevented us from purifying it thoroughly, as sublimation, which had given the substance melting at 185°, turned out to be too wasteful a process for working up large amounts; we were not surprised, therefore, that our analysis of the silver salt gave 62.82 per cent. of silver, instead of the 64.69 per cent. calculated for argentic tartronate. This result, however, bad as it is, comes nearer to that for argentic tartronate than to that for any other substance which could well be formed, and therefore gives us the desired confirmation.[2] The small amount of tartronic acid obtained, less than 0.5 gram from about 10 grams of the oil, may be accounted for on the supposition that the larger part of the tartronic acid was decomposed by the strong hydrochloric acid used in the saponification of the oil, as Conrad and Bischoff[3] have observed that tartronic acid is decomposed very easily by hydrochloric acid, and we also were unable to obtain a trace of the acid from the filtrate after argentic chloride had been precipitated from the silver salt by a slight excess of hydrochloric acid. In fact, we should not have thought it worth while to try to obtain tartronic acid by the action of hydrochloric acid on our oil, if it had not been for the fact that tartronic ester has been made from calcic tartronate by the action of hydrochloric acid gas and alcohol,[1] which would seem to show that the tartronic acid is more stable in presence of strong than of dilute hydrochloric acid, improbable as this sounds. This view is in harmony with our observations detailed above, and Conrad and Bischoff state that even very dilute acid decomposes it readily; but even granting this, a large proportion of the tartronic acid must have been decomposed during the treatment with hydrochloric acid, and this seems to us sufficient to make it more than probable that the tartronic acid is the product of the principal reaction, and not formed in a secondary one taking place only to a limited extent. If this is admitted, the following reactions would give the most probable explanation of what takes place:

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[1] Ann. Chem. (Liebig) **209**, 222 (1881).

[2] No attempt was made to obtain a better analysis of the tartronic acid, because the work upon the corresponding trinitro compound described in another paper furnished a complete confirmation of the theory of the reactions given here.

[3] Ann. Chem. (Liebig) **209**, 223 (1881).

I. $C_6HBr_3(NO_2)_2 + NaCH(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaBr.$
II. $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaCH(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$
III. $C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.$
IV. $NaCH(COOC_2H_5)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2.$
V. $CHBr(COOC_2H_5)_2 + NaOH = CHOH(COOC_2H_5)_2 + NaBr.$

Of these reactions, I, II, and III take place before, IV and V after, the addition of the water used in working up the product. That Reaction III takes place we infer from our discovery of tartronic acid among the products of saponification of the oil, as Conrad and Bischoff[2] have proved that brommalonic ester is decomposed by sodic hydrate, according to Reaction V.[3]

The experiments of one of us with G. D. Moore upon the action of sodium malonic ester on tribromtrinitrobenzol have shown that these reactions take place in a way analogous to that just worked out. For the details we would refer to the paper on this subject.

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[1] Freund, Ber. d. chem. Gesell. **17**, 786 (1884). Pinner, ibid. **18**, 757 (1885).

[2] Ann. Chem. (Liebig) **209**, 222 (1881).

[3] A fuller discussion of these reactions will be found in the general paper at the end of this series.

The objection which might be raised against these reactions, that the yield of bromdinitrophenylmalonic ester is at best only about 50 per cent. of that required by theory, and therefore that some other substance may be formed from the tribromdinitrobenzol in addition to it, is disposed of by the fact that on making the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by exactly analogous reactions, the yield rose to 80 per cent. of the theoretical. It follows, therefore, that the 47 to 50 per cent. unaccounted for in our preparations remained dissolved in the oily secondary product; but although we have made many attempts to recover it, none of them have been crowned with success.

Saponification of Bromdinitrophenylmalonic Ester.

In our previous paper we stated that strong hydrochloric acid decomposed bromdinitrophenylmalonic ester, when the two substances were heated together to 140°–145° in a sealed tube, and described the product formed, stating, however, that all our results up to that time must be regarded as preliminary. Upon taking up the subject again, we studied in the first place the gas evolved when the tube was opened, and found that, in addition to the gas already mentioned burning with a green-bordered flame (which is undoubtedly ethyl chloride), carbonic dioxide was given off, as was proved by the precipitate formed when the gas was passed through lime-water. It is to be observed, however, that if the temperature to which the tubes were heated was 140°, or a little lower, very little, if any, carbonic dioxide was given off, and the product insoluble in the hydrochloric acid was oily; on the other hand, when a crystalline product was obtained at a somewhat higher temperature, carbonic dioxide was given off freely. We next attempted to prepare the substance in open vessels by substituting for strong hydrochloric acid dilute sulphuric acid boiling at about the temperature to which we heated the tubes, and found that not only did we obtain the product in this way, but that it was much purer than that made in the sealed tubes with hydrochloric acid. We have arrived accordingly at the following method as the most convenient for saponifying the bromdinitrophenylmalonic ester. 2 grams of the ester are mixed with about 100 cc. of dilute sulphuric acid, specific gravity 1.44 and boiling point 132°, and the mixture boiled in a flask with a return condenser, until the oily drops of melted bromdinitrophenylmalonic ester have all gone into solution, which usually takes about an hour and a half. After this the solution, as it cools, deposits long, pale yellow needles of the new substance, which, if the preparation has succeeded well, melt at 177° at once. If, however, the action has not run so well, and the melting point is somewhat lower than this, the substance can be easily purified by crystallisation from boiling water acidified with a few drops of dilute sulphuric acid, but in no case should it be crystallised from pure water, or alcohol, as these solvents decompose it in the curious way described later in this paper, when we consider its properties.

Metabromdinitrophenylacetic Acid, $C_6H_2Br(NO_2)_2CH_2COOH$.

The substance prepared in the manner just described, and showing the constant melting point 177°, was dried at 100°, and analysed with the following results:

I. 0.2106 gram of the substance gave on combustion 0.2426 gram of carbonic dioxide and 0.0420 gram of water.

II. 0.1933 gram of the substance gave 15.6 cc. of nitrogen at a temperature of 15°.5 and a pressure of 759.2 mm.

III. 0.1821 gram of the substance gave, according to the method of Carius, 0.1152 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2H$.	Found.		
		I.	II.	III.
Carbon	31.47	31.43		
Hydrogen	1.64	2.21		
Nitrogen	9.18		9.42	
Bromine	26.23			26.93

These analyses supersede those already published,[1] which were made with a substance prepared by crystallisation from dilute alcohol, before we had found that this solvent decomposed the compound; it was therefore decidedly impure, as indeed was shown by its melting point, which was 170° instead of 177°.

The yield of the bromdinitrophenylacetic acid is essentially quantitative, as two grams of the bromdinitrophenylmalonic ester gave, after treatment with dilute sulphuric acid, 1.4 grams of bromdinitrophenylacetic acid melting at 177°, instead of the calculated amount, 1.56 grams, that is, 90 per cent. of the theory; the missing 10 per cent. without doubt remained dissolved in the dilute sulphuric acid, in which the substituted acetic acid is not wholly insoluble, as the 1.4 grams were obtained by simple filtration, no attempt being made to recover the organic substance from the filtrate.

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[1] Proceedings Am. Acad. 24, 11 (1889).

In view of the observations described above, there can be no doubt that the following reactions take place when bromdinitrophenylmalonic ester is saponified by heating it with hydrochloric acid at temperatures in the neighborhood of 145°:

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2 + 2HCl =$$
$$C_6H_2Br(NO_2)_2CH(COOH)_2 + 2C_2H_5Cl =$$
$$C_6H_2Br(NO_2)_2CH_2COOH + CO_2 + 2C_2H_5Cl.$$

And there can be no question that a similar reaction takes place when dilute sulphuric acid is substituted for strong hydrochloric acid. In fact, this was so obvious that we have not thought it worth while to try to isolate the sulphovinic acid which must be formed in this case instead of the ethylchloride.

Properties.—The metabromdinitrophenylacetic acid crystallises from an aqueous solution containing a little sulphuric acid in yellowish white needles, often one or two centimeters long, which appear under the microscope as tolerably thick prisms frequently tapering owing to modification by the planes of a pyramid with a very acute angle, but almost always, even in addition to this tapering, terminated bluntly by the planes of another very obtuse pyramid. Occasionally the termination is a single plane at a moderately acute angle to the sides, but this looked as if it were due to cleavage. The crystals are generally very well developed, but if they are small, a tendency to twin longitudinally is observed. If the substance is crystallised from alcohol, the forms like feathers, or half-feathers, described in our previous paper, and groups of branching needles looking like certain feathery seaweeds, appear; but as the alcohol decomposes the substance, these forms can hardly be ascribed to the substituted acetic acid itself. It melts at 177°, and is essentially insoluble in ligroine or carbonic disulphide; very slightly soluble in chloroform, slightly in benzol, more soluble in both of these solvents when hot; tolerably soluble in ether, separating from the solution in a liquid form, which solidifies on stirring; easily soluble in acetone or glacial acetic acid; soluble in cold alcohol, more freely in hot, but the alcohol decomposes it, as is indicated by the change in the appearance of the crystals, the long yellowish prisms of unaltered bromdinitrophenylacetic acid becoming roughly studded with fine needles of another substance, and by the lowering of the melting point, when the substance is crystallised from alcohol; evaporation to dryness of the alcoholic solution, if repeated three times, reducing the melting point from 177° to 147°; while after two more evaporations, making five in all, the melting point had sunk to 103°-104°, at which point it remained constant after repeated crystallisation. The substance obtained in this way crystallised in rectangular prisms, or plates, was not acted on by alkalies, and was recognised as Grete's metabromdinitrotoluol.[1] For greater certainty it was analysed, with the following results:

I. 0.1690 gram of the substance gave, by the method of Carius, 0.1210 gram of argentic bromide.

II. 0.2185 gram of the substance gave 20.3 cc. of nitrogen at a temperature of 22°.5 and a pressure of 773.3 mm.

	Calculated for $C_6H_2Br(NO_2)_2CH_3$.	Found. I.	 II.
Bromine	30.65	30.47	
Nitrogen	10.73		10.69

This conversion of the metabromdinitrophenylacetic acid into the corresponding toluol by boiling with alcohol, when it is so stable in presence of boiling dilute sulphuric acid, seemed to us so interesting that we have examined it more carefully. Having in the first place determined that the alcohol was neutral to test papers, to prove that the reaction could not be due to a trace of alkali, or acid in it, a quantity of the substance melting at 177° was boiled in a flask under a return condenser with a little alcohol for three hours, and pure air occasionally drawn through the apparatus to sweep out its contents into a set of absorption bulbs filled with lime-water; in this way a heavy precipitate was obtained, which consisted in great part of calcic hydrate precipitated by the alcohol vapor, but also contained calcic carbonate, as was shown by effervescence when it was dissolved in an acid, thus proving that carbonic dioxide had been given off. The alcoholic solution, after it had been boiled for an hour and a half longer, gave crystals, melting at 103° to 104°. It seems evident, therefore, that the reaction runs as follows:

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[1] Ann. Chem. (Liebig) **177**, 258 (1875).

$$C_6H_2Br(NO_2)_2CH_2COOH = C_6H_2Br(NO_2)_2CH_3 + CO_2,$$

and the alcohol seems to take no part in it. Methyl alcohol, in which the substance is more soluble than in ethyl alcohol, brings about a similar decomposition, but more slowly. In boiling water the metabromdinitrophenylacetic acid is tolerably soluble, but nearly insoluble in cold water. The decomposition produced by alcohol also takes place when the aqueous solution is boiled, but very slowly, so that long boiling is necessary to convert the substance completely into the substituted toluol; nevertheless, after distilling with steam for several hours, the whole of the substance had passed over into the receiver as metabromdinitrotoluol, since none of the substituted acetic acid, which does not distill with steam, was left in the flask. The presence of a very small amount of sulphuric acid (two or three drops of the dilute acid to 100 cc. of water) is sufficient to prevent this decomposition entirely, as a specimen of the substituted acetic acid showed no signs of decomposition, even after having been distilled with steam for three hours with only the amount of dilute sulphuric acid which remained adhering to it after the excess of acid used in its preparation had been removed by filtration. The best solvent for the bromdinitrophenylacetic acid, therefore, is boiling water containing a few drops of sulphuric acid. If the substance has become contaminated with the substituted toluol, it can be purified conveniently by distillation with steam in presence of a few drops of sulphuric acid, when the toluol passes over, and the acetic acid remains behind in the flask.

Ammonic hydrate dissolves the metabromdinitrophenylacetic acid, forming a colorless solution if the acid is in excess; but if the ammonic hydrate is added in slight excess, a green solution is obtained, which turns dark brown if a large excess of ammonic hydrate is added, but regains its green color on dilution with water. Both the colorless and green solutions smell of ammonia, and this smell could not be removed by gentle boiling, or by allowing the solution to stand over sulphuric acid, from which we infer that the ammonium salt is a decidedly unstable substance. When either solution is warmed on the water-bath for some time it is partially decomposed with formation of a precipitate of metabromdinitrotoluol, and the green solution turns yellow even when allowed to evaporate spontaneously. Hydrochloric acid threw down from the solution a precipitate of metabromdinitrophenylacetic acid. The ammoniacal solution, prepared with an excess of the acid and freed as completely as possible from an excess of ammonia, gave no precipitate with baric, strontic, or calcic chloride, but with the salts of many of the heavy metals it gave precipitates, of which the following were the most characteristic:

Aluminic chloride, heavy, white.
Ferric chloride, heavy, very pale buff.
Cupric sulphate, heavy, pale blue.
Mercuric nitrate, heavy, yellowish white.
Mercuric chloride, a very slight precipitate, probably white precipitate from the slight excess of ammonic hydrate.
Mercurous nitrate, heavy, white.
Plumbic acetate, heavy, white.
Argentic nitrate, heavy, white.

The behavior with argentic nitrate is especially characteristic; if the solutions are strong, the mixture becomes nearly solid from the formation of a white flocculent precipitate, which frequently swells up, forming a little heap or pyramid, and after standing for some hours becomes converted into good-sized crystals. The analysis and properties of this salt are described more in detail below.

With sodic hydrate a solution of the acid turns a deep Prussian green color, which passes in time into a yellowish brown, this latter color appearing at once when an excess of sodic hydrate is added. If the green solution is acidified, a precipitate is obtained, which, although nearly colorless when dry, becomes purple when moistened with alcohol. This precipitate was oily at first, and, although it solidified later, we did not succeed in finding any solvent from which it could be crystallised. That the sodic hydrate had acted on the bromine was shown by an actual experiment, which gave the following results:

0.67 gram of the acid yielded by treatment with sodic hydrate so as to form the green salt, 0.1136 gram of argentic bromide, which corresponds to 0.0483 gram of bromine instead of the 0.1757 gram contained in the amount of acid taken; that is, 27.5 per cent. of the whole had been removed.

The yellowish brown solution obtained, when a large excess of sodic hydrate was used, or the mixture of sodic hydrate and metabromdinitrophenylacetic acid was boiled for some time, gave on addition of an acid a viscous red substance, which was exceedingly unmanageable. That bromine was removed in quantity in this way is shown by the following determination:

0.2412 gram of the metabromdinitrophenylacetic acid was boiled with sodic hydrate for three-quarters of an hour; the product, after acidifying with nitric acid, and filtering out the precipitate, gave 0.1180 gram of argentic bromide, corresponding to 0.0502 gram of bromine instead of the 0.0632 gram contained in the weight of acid taken; that is, 79.4 per cent. of the whole.

It is evident, therefore, that the original compound has undergone a deep-seated alteration, and the new crimson substance is probably a phenol. This view of its nature receives some confirmation from the fact that it is decomposed with the greatest ease by even somewhat dilute nitric acid. We have not yet succeeded in bringing either of the products derived from sodic hydrate into a state fit for analysis, although the slight solubility of the barium salt of the crimson acid awakened hopes of success; but these ended in disappointment, as the salt proved quite as viscous as the free acid.

Potassic carbonate gives with the metabromdinitrophenylacetic acid results similar to those obtained with sodic hydrate, but less marked.

We hoped to be able to throw some light on this action of alkalies on the metabromdinitrophenylacetic acid by the study of the corresponding anilido compound, but have not succeeded as yet in preparing it, as aniline converts the free acid direct into metanilidodinitrotoluol,[1] $C_6H_2CH_3(C_6H_5NH)(NO_2)_2$, melting point 142°, and the saponification of anilidodinitrophenylmalonic ester with sulphuric acid yielded only uninviting viscous products.

Radziszewski,[2] Gabriel and R. Meyer,[3] and Heckmann,[4] have prepared a dinitrophenylacetic acid which differs from that just described only in containing no bromine. This substance also loses carbonic dioxide easily, passing into dinitrotoluol, but none of the chemists who have worked with it describe a decomposition by solvents similar to that observed by us; in fact, they crystallised it for analysis from boiling water, but, as in all their methods of preparation acids were used, it is possible that a sufficient amount of sulphuric acid was present during the crystallisation to prevent the decomposition. It appears that none of them tried to crystallise it from alcohol. The statement is made, however, that the sodium or potassium salt of the acid decomposes slowly on standing, instantly on boiling, giving carbonate and dinitrotoluol; from this it would seem probable that our bromine acid was more stable than that containing no bromine, as our ammonium salt (the sodium or potassium salt could not be obtained) stood unaltered for many days, and even could be warmed on the water-bath for some minutes with only slight decomposition. The curious change of color with sodic hydrate observed by us did not occur with the dinitro body, confirming our conclusion that this action was due to the removal of bromine by the sodic hydrate.

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[1] Hepp, Ann. Chem. (Liebig) **215**, 371 (1882).

[2] Ber. d. chem. Gesell. **2**, 210 (1869).

[3] Ibid. **14**, 823 (1818).

[4] Ann. Chem. (Liebig) **220**, 134 (1883).

Argentic Metabromdinitrophenylacetate,
$C_6H_2Br(NO_2)_2CH_2COOAg.H_2O$.

This substance was prepared by adding a solution of argentic nitrate to a solution of the acid in ammonic hydrate, which had been freed from the excess of ammonia as completely as possible, best by using an excess of the acid in preparing the salt. The heavy flocculent precipitate, which, if the solutions were strong, entirely filled the liquid, and even piled up above its surface, became crystalline on standing, and was purified by washing with cold water. Some of the salt is also formed when argentic nitrate is added to an aqueous solution of the free metabromdinitrophenylacetic acid. The analysis of the salt gave the following results.

0.3530 gram of the air-dried salt lost, when heated to 100°, 0.0149 gram.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag.H_2O$.	Found.
Water,	4.19	4.22

I. 0.1674 gram of the salt dried at 100° gave, after being heated with fuming nitric acid in a sealed tube[1] and precipitated with potassic bromide, 0.0761 gram of argentic bromide.

II. 0.1556 gram of the salt treated in the same way gave 0.0707 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag$.	Found.	
		I.	II.
Silver,	26.21	26.11	26.10

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[1] We had hoped in this way to determine both the silver and bromine in one operation, but found that the filtrate gave a precipitate with potassic bromide. It would seem, therefore, that the presence of an excess of argentic nitrate is necessary to retain all the bromine.

Properties.—The argentic bromdinitrophenylacetate forms white flat prisms terminated by a single plane at an oblique angle; the terminated end is somewhat broader than the other, so that the crystals look like a flattened base-ball bat. They have also a tendency to twin longitudinally. When put in the flame of a Bunsen lamp they burn with a sparkling flame, but when heated carefully on a piece of porcelain decompose quietly, leaving a residue of silver. The substance is very slightly soluble in cold water, so that it can be washed without too great loss; more soluble in hot water, from which it crystallises apparently without decomposition; insoluble in cold alcohol, but slowly decomposed if heated with it.

Constitution of Bromdinitrophenylmalonic Ester.

The formation of metabromdinitrotoluol from bromdinitrophenylmalonic ester by a series of reactions giving essentially a quantitative yield and taking place at temperatures not above 150°, throws a great deal of light on the nature of this substance. In the first place, its conversion into a toluol derivative is a welcome confirmation of the formula which we have given it, and which did not rest on the most secure experimental foundations. In our first paper it was stated that the analysis left the choice open between the following formulas,

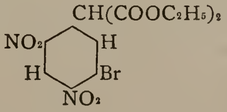
I. $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$,
II. $C_6HBr(NO_2)_2C(COOC_2H_5)_2$,

and we decided in favor of the first on account of the analyses of the sodium salt, an amorphous substance for the purity of which we had no guarantee, and also on account of the ease with which this salt was formed and decomposed, the product of the decomposition being the original ester. Against this formula stood only our inability at the time to explain the reactions by which it was formed, an objection which is removed by this paper. The easy conversion of a substance having Formula I into a toluol compound is to be expected, whereas with one having Formula II it would be necessary to add two atoms of hydrogen, an action which could hardly take place quantitatively by boiling with dilute sulphuric acid, or distillation with steam, the two processes employed in converting the bromdinitrophenylmalonic ester into the bromdinitrotoluol. This formation of the substituted toluol therefore establishes Formula I beyond question.

In the second place, the way is opened to the determination of the position of the substituting radicals upon the benzol ring in all these compounds, as their position must be the same as in the bromdinitrotoluol. Messrs. W. B. Bentley and W. H. Warren have accordingly, at our request, determined the constitution of the bromdinitrotoluol by replacing its bromine successively by the amido group and by hydrogen, and have found in this way that its constitution is

$$CH_3 . Br . NO_2 . NO_2 . 1 . 3 . 4 . 6.$$

For the details of their work we would refer to their paper which will follow the present one. It follows from this that in the tribromdinitrobenzol $Br.H.Br.NO_2.Br.NO_2.1.2.3.4.5.6$, the bromine numbered 1, which stands in the ortho position to one nitro group and the hydrogen, in the para position to the other nitro group, has been replaced by the malonic ester radical $CH(COOC_2H_5)_2$; that the bromine replaced by hydrogen is the one between the two nitro groups; and that the third bromine, which is in exactly the same relation to the nitro groups as the one replaced by the malonic ester radical, is left entirely unaltered. This last fact seems very strange to us. The constitution of our bromdinitrophenylmalonic ester is therefore represented by the following graphical formula:



Contributions from the Chemical Laboratory of the Department of Agriculture.

XIV.—ANALYSES OF THE SEED OF CALYCANTHUS GLAUCUS.

By H. W. Wiley.

Botanical Data.

Natural Order Calycanthaceae. Shrubs, with opposite, simple, entire, exstipulate leaves. Flowers purple, sometimes pale, sweet-scented, solitary, terminating short branches. Sepals and petals similar, indefinite, united below into an inversely conical cup. Stamens indefinite, inserted on the inner margin of the cup. Pistils distinct, indefinite, one or two ovuled, inserted on the sides and bottom of the cup within. Fruit made up of one to many achenia enclosed in the enlarged calyx-cup. Species four, all American.

C. floridus, L. Leaves oval to oblong, softly downy beneath. Rich uplands from North Carolina to Mississippi.

C. glaucus, Willdenow. Leaves oblong-ovate to ovate-lanceolate, conspicuously taper-pointed, glaucous beneath, roughish above. North Carolina to Georgia, in the mountains.

C. laevigatus, Willdenow. Leaves oblong, either blunt or taper pointed, bright green and glabrous or nearly so on both sides. Flowers 1 to 1½ inches long. Pennsylvania and southward along the Alleghanies.

C. occidentalis, Hooker & Arnott. Leaves of the form of C. laevigatus, not shining beneath, glabrous above. Flowers one inch or more long. Northern California and northward.

The seeds are in pods, from eight to sixteen in each pod.

The weight of one hundred seeds unhulled was found to be 21.1964 grams. The average weight of each seed is therefore about 200 milligrams.

In preparing the seeds for analysis they were first removed from the pod and then carefully hulled. The pods, hulls and kernels were examined separately.

The pods and hulls were ground in a drug mill and passed through a ½ mm. mesh sieve. On account of the great quantity of oil in the kernels it was found impracticable to treat them as described above. They were therefore reduced to as fine a powder as possible on an iron plate ore pulveriser and the oil removed by petroleum spirit. After the removal of the spirit the deoleated residue was ground to a fine flour and passed through a ½ mm. mesh sieve.

The analyses of the pod, hull and kernel gave the following data:

Composition of the Pod.

	Per cent.
Moisture,	9.03
Petroleum spirit extract,	3.07
Sulphuric ether extract,	3.25
Absolute alcohol extract,	1.73

	Per cent.
80 per cent. alcohol extract,	1.87
Fibre insoluble in dilute acid and alkali,	29.26
Albuminoids,	5.25
Ash,	4.24
Digestible fibre, starch and undetermined, by difference,	42.26

Composition of the Hulls.

	Per cent.
Moisture,	11.39
Petroleum spirit extract,	1.22
Sulphuric ether extract,	0.30
Absolute alcohol extract,	0.54
80 per cent. alcohol extract,	1.09
Albuminoids,	2.63
Fibre insoluble in dilute acid and alkali,	30.71
Ash,	1.72
Digestible fibre, starch, etc. (by difference),	50.40

Composition of the Unextracted Kernels.

	Per cent.
Moisture,	5.36
Petroleum spirit extract,	47.08
Ether extract,	1.29
Absolute alcohol extract,	9.69
80 per cent. alcohol extract,	2.48
Fibre,	1.36
Ash,	1.08
Albuminoids,	23.62
Digestible fibre, starch, and by difference,	8.05

Composition of the Extracted Kernels.

	Per cent.
Moisture,	3.52
Petroleum spirit extract,	3.64
Ether extract,	0.31
Absolute alcohol extract,	17.33
80 per cent. alcohol extract,	6.33
Fibre,	2.85
Ash,	4.69
Albuminoids,	42.31
Digestible fibre, starch, and by difference,	13.00

The above data show that the kernel of the calycanthus possesses remarkable qualities. The small quantity of undetermined substances is not remarkable when it is remembered that a considerable quantity of albuminous matter is extracted by alcohol, and is therefore counted twice in the summary. The same remark may be applied to the alkaloid present in the seed which will be described further on. The almost entire absence of starch is a noteworthy characteristic of the calycanthus flour. When a small portion of it is boiled with water, cooled and treated with a solution of iodine, only a faint reaction is produced. Starch is therefore present in extremely small quantities.

The percentage of oil is very large. Dr. Eccles, to whose discovery of the alkaloid I will soon refer, reported 39 per cent. of oil. We found in most careful extractions with petroleum spirit, over 47 per cent. Add to this the portion given up to ether and it is seen that practically the hulled seed is one-half ether extract. The character of this oil is described further on.

The large proportion of albuminoids is also a marked property of the seed. It contains nearly twice as much of this valuable substance as wheat.

The quantity of sugar (dextrose, sucrose and dextrine) in the seed is also large, and from the analysis it is easy to see why the "bubby" berries are so greedily sought after by cattle.

The separation and determination of the different sugars has not yet been completed.

Oil from Calycanthus Seed.

The oil from calycanthus seed has a beautiful faint yellow color, and when extracted with an appropriate solvent and purified, a peculiar odor.

The specific gravity of the purified oil, extracted by petroleum spirit, compared with water at the boiling point, was found to be .9058. The specific gravity of the expressed oil in similar conditions was .9110. The higher specific gravity of the expressed oil was doubtless due to a trace of moisture which it contained, it having been simply warmed and filtered before the specific gravity was taken.

Five grams of the oil tested for volatile acid showed the absorption of only .2 cc. of N/10 barium hydrate solution. The oil may therefore be said to be entirely free from volatile acids.

The iodine absorption of the oil was found to be as follows:

For the crude expressed oil, 129.53 per cent.; for the purified extracted oil, 128.66 per cent. In respect of its iodine coefficient, therefore, calycanthus oil occupies a mean position between cotton and flaxseed oils.

The crystallising point of its fatty acid was found to be 12.5°.

Judging by its iodine coefficient, calycanthus oil would be a mild drying oil, but no experiment to determine this point has yet been made. The iodine absorption being so much greater than would be required for olein alone, shows the presence of lin-oleic acid or some homologue thereof.

The refractive index of the oil determined by the Pullfrick refractometer at 28° is 1.47351. The index of pure water determined at the same degree is 1.33338.

The Alkaloid in Calycanthus Seed.

Dr. R. G. Eccles, of Brooklyn, N. Y., has discovered in the seed of the calycanthus an alkaloid which he has named calycanthine. His attention was called to this substance by a paper of E. E. Sterns on "The Fruit of Calycanthus," published in the "Bulletin of the Torrey Botanical Club," for August, 1888, p. 205. The poisonous character of these seeds was called to the attention of Mr. Sterns by Mr. J. H. H. Boyd, of Cagle, Tenn., in a letter written November, 1887. Mr. Boyd's letter is as follows:

"Hundreds of cattle and sheep have died here in the past five years from 'bubby' (the eccentric name of the shrub). The seeds only are poisonous. When a brute gets a sufficient dose, from five to ten well-filled pods, it makes for the nearest water and often falls dead while drinking, or it may live three or four weeks and then die. The symptoms are like those of a man extremely drunk, except that any noise frightens it. Stamp the ground hard close to a brute poisoned with 'bubby,' and it will jump and jerk and tremble for several minutes. That is our method of telling when they have taken it. The eyes turn white and glassy, and while lying they throw back the head and look as if dead already. 'Bubby' does not seem to hurt a brute so much if it cannot get water. Our best remedy is apple brandy, strong coffee and raw eggs poured down as soon as possible after finding. It is certain that 'bubby' is the most poisonous of any shrub or weed in existence here, from the fact that when brutes have once eaten it they will take it every time they can get it. It grows on every hillside, along all branches (creeks), in every fence corner and almost everywhere."

Dr. Eccles' first paper was published in the "Western Druggist" of January, 1889, on p. 15. The alkaloid in the seeds is evidently not a very virulent one, since twenty of the seeds were eaten without any toxic symptoms being manifested. The alkaloid is described in this paper as being slightly soluble in water and very soluble in ether or chloroform. Its salts are insoluble in the latter substance, but very soluble in water. Its most characteristic color is the development of a green color on the addition of strong nitric acid. A second paper by Dr. Eccles was published in the "Druggist's Circular and Chemical Gazette" for March, 1888, on p. 65. He describes the method of extracting the alkaloid as that of Dr. Lyons.

"The finely powdered seeds were first macerated for twenty-four hours, with occasional shaking in a mixture of ether, alcohol and ammonia. After allowing the mixture to settle, the clear solution was decanted and evaporated to a small bulk, then stirred or shaken with dilute sulphuric acid and concentrated ether. This was again evaporated until all the ether was gone, when it was filtered. The clear acid solution was neutralised with ammonia shaken up with ether, allowed to settle, the ether decanted from the surface into a porcelain evaporating basin, where it was allowed to spontaneously evaporate and leave the alkaloid. This alkaloid, for several hours after the last of the ether had gone, had a strong, distinct odor of pyridine, so that it was probably contaminated with that volatile alkaloid of tobacco."

The alkaloid in some of the seed having first been extracted by alcohol until it gave no further test, it was treated with a little sulphuric acid, by which an additional alkaloid was extracted, leading Dr. Eccles to suppose the existence of more than one in the plant. Dr. Eccles also states that the acid solution of the alkaloid precipitated by ammonia did not yield the alkaloid by shaking with ether, an experience which is entirely contrary to my own. About 2 per cent. of the alkaloid was found by Dr. Eccles.

Mr. Boyd wrote to the Department in March, 1889, for information in regard to the calycanthus poison, and at his instigation I communicated with Dr. Eccles on the subject. He kindly gave me all the information which he had in regard to the matter, and under date of March 20, 1889, wrote as follows:

"I hated to give the investigation up, as it has just reached the most interesting point, but you know the saying, 'man proposes and God disposes.' After the rush is over, say some three months hence, I will do some work on the subject, and would therefore beg you to let me know from time to time what you discover."

Since that time I have not seen any report of any further work of Dr. Eccles, and my contribution at the present time is certainly not intended to take the place of any investigation which he has made or may make in the matter. The methods which I used in isolating the alkaloid are as follows:

Alkaloid in Extracted Oil. Since nearly all the alkaloids are more or less soluble in fixed oil, I was led to suppose that the calycanthus seed, containing so large a percentage of fixed oil, might yield some of its alkaloid to that oil on extraction with petroleum spirit. To see if this assumption were true, a portion of the extracted oil, after being freed as nearly as possible from petroleum, was shaken with an equal volume of dilute sulphuric acid (1 to 50) and the acid liquid separated from the oily layer. This acid solution was shaken with petroleum ether to remove any fat which it might contain. The residual acid solution was made strongly alkaline with ammonia and shaken with ether. The ethereal solution was evaporated and the alkaloid thus obtained dissolved in dilute sulphuric acid, and treated with a solution of iodine in potassium iodide. A dense brown precipitate indicated the presence of an alkaloid.

500 grams of the oil were next washed with 1000 cc. of dilute sulphuric acid (1 to 50) in successive portions. The acid washings were shaken with petroleum to remove any trace of oil. The solution was then made strongly alkaline with ammonia and shaken four times with 150 cc. of ether. The ether was evaporated in a tared dish, and the extract dried at 100° was found to weigh .1366 gram. The percentage of alkaloid, therefore, in the oil was .027.

The above reaction shows that the amount of alkaloid extracted by the oil, when the latter is removed by petroleum ether from the seed, while important from a chemical point of view, would not appreciably affect the quantitative determination of the alkaloid in the seed.

Alkaloid in the Seed. The seeds were carefully removed from the hulls and the two substances examined separately for alkaloids and bitter principles.

Alkaloid in the Kernel. The seeds removed from the hulls were powdered as finely as possible, considering their oily state. The fat was then extracted by means of petroleum spirit. The dry residue was finely powdered and passed through the fine mesh sieve employed in the preparation of vegetable substances for analysis. 10 grams of the powdered seed were then weighed into each of six flasks. The first flask was treated with 100 cc. of ether; the second with 100 cc. of alcohol, 95 per cent.; the third flask with 100 cc. of chloroform; the fourth with a mixture of ether, alcohol and ammonia; the fifth with 100 cc. of dilute sulphuric acid (1 to 50); the sixth flask with equal parts of ether and alcohol. The flasks were all tightly corked and placed in a warm room, the temperature of which was 35°. They were shaken at frequent intervals for four days, and then treated as follows:

The liquid portions of Nos. 1, 2, 3, 4 and 6 were filtered into evaporating dishes, and the filter papers containing a portion of the solid substance were returned to the flasks. The same quantity of the reagents was again added and the flasks treated in the same way as indicated. The residue was then washed with frequent shaking by the same quantity of the particular reagent used for each one. The finely powdered seed was thus extracted for six days with the solvents, and washed thoroughly with the same solvent.

No. 5, containing the sulphuric acid reagent, was found to be in the state of an emulsion. It was therefore found impossible to filter off the liquid portion. The whole mass was made strongly alkaline with ammonia, and treated at once with 200 cc. of ether. The emulsion separated very slowly, but after its separation the ether layer was poured off into an evaporating dish and evaporated to dryness. This treatment with ether was repeated eight times, and the whole of the ethereal solution evaporated in the same dish. Abundant crystals of the alkaloid were shown by the first evaporation. The alkaloidal extracts from all the samples were then treated as follows:

They were thoroughly washed in successive portions of dilute sulphuric acid (1 to 50), about 100 cc. of the acid being used in all. The acid washings were then shaken in a separatory tube twice with 50 cc. of ether, and the ethereal layer removed. In this way the solution was freed entirely of fat and other substances soluble in ether, including, perhaps, a trace of the sulphate of the alkaloid. The remaining portion was now made strongly alkaline with sodic hydrate, and shaken with successive portions of ether of about 50 cc. each for five times. The extracts, which were now in a very pure state, with exception of No. 1, were evaporated to dryness in tared glass dishes and weighed. The percentages of alkaloid obtained by the six different methods were as follows:

No. 1,	0.79	per cent.	alkaloid,	very	impure.
" 2,	1.20	"	"	"	pure.
" 3,	1.85	"	"	"	"
" 4,	2.35	"	"	"	"
" 5,	4.25	"	"	"	"
" 6,	0.22	"	"	"	"

In No. 4, only one extraction of four days was made. In treating the residue the second time with 100 cc. more of the same reagent the flask was broken. The high percentage obtained shows that this method of extraction completed would have yielded almost as large a percentage of the alkaloid as was obtained in No. 5.

The residue from Nos. 1, 2, 3 and 6, of the above samples, were treated with dilute H_2SO_4 for twenty-four hours, filtered out, and re-extracted with same reagent. The acid solutions were treated as in No. 5, and the percentages of alkaloid obtained were as follows:

No. 1,	1.98	per cent.	alkaloid,	pure.
" 2,	0.76	"	"	"
" 3,	1.30	"	"	"
" 6,	1.83	"	"	"

The alkaloid thus extracted by H_2SO_4 did not show any difference in composition from the other extracts.

Another extraction was made by forming a paste of the flour with lime, and extracting with an equal mixture of ether and alcohol under pressure at 80°. The percentage of alkaloid obtained by this treatment was 2.58 (alkaloid pure). The residue was neutralised and treated as in the other cases by dilute H_2SO_4. The percentage of alkaloid obtained was 0.39 per cent.

The percentages of total alkaloid obtained in all extractions were:

No. 1,	2.77	per cent.
" 2,	1.96	"
" 3,	2.15	"
" 4,	2.35	"
" 5,	4.25	"
" 6,	2.05	"
" 7,	3.07	"

General Properties of the Alkaloid.

Calycanthine crystallises from ether in feathery masses on the sides of the dish, presenting the appearance of a diminutive pine forest. These feathery crystals form very rapidly and present a beautiful appearance. On slower evaporation the bottom of the dish is found to be covered with triangular crystals which appear to be hemihedrae from oblique octohedrae. The exact crystalline structure will be shortly determined.

Specific Rotatory Power.

The alkaloid being practically insoluble in alcohol and water, the determination of its specific rotatory power is deferred until the properties of its salts can be studied.

Percentage Composition.

The following numbers were obtained for the percentages of the elementary substances present in the alkaloid:

Carbon, ...	42.13	per cent.
Hydrogen, ...	7.75	"
Nitrogen, ...	16.22	"
Oxygen (by difference), . .	33.77	"

The above figures lead to the following formula for calycanthine, $C_{18}H_{40}O_{11}N_6$.

	Calculated for $C_{18}H_{40}O_{11}N_6$.		Found.	
C	41.86	per cent.	42.13	per cent.
H	7.75	"	7.89	"
N	16.28	"	16.22	"
O	34.11	"	33.76	"

Alkaloid in the Hulls. Ten grams of the hulls were examined for alkaloids by extraction with dilute H_2SO_4 and subsequent treatment as indicated above.

The percentage obtained was .83. The alkaloidal principle was amorphous, but contained traces of calycanthine as revealed by the color tests to be mentioned. The nature of the amorphous alkaloidal principle has not yet been determined.

Color Reactions. Calycanthine exhibits the most remarkable series of color tests of any known alkaloid.

Dr. Eccles described the beautiful green color produced by nitric acid. In extending these tests I obtained the following results:

H_2SO_4, pale yellow.

HNO_3, bright green (persistent).

$H_2SO_4 + C_{12}H_{22}O_{11}$, (sucrose) fine purple (persistent and changing finally to blue).

$H_2SO_4 + K_2Cr_2O_7$, fine blood-brick red.

Dextrose, maltose, etc., gave also the furfurol reaction, but without so marked a purple as with sucrose.

The presence of sugar in the seed renders it possible to secure the furfurol reaction in the raw seed by the simple application of H_2SO_4.

The examinations necessary to complete the investigations, and to determine the crystalline forms of the alkaloids and the properties of its compounds with common acids, will be made at as early a date as possible. We hope also to be able to study its physiological effects.

In these investigations I have been assisted by Messrs. Horton, Trescott, Krug and Sanborn.

ON A VOLUMETRIC METHOD OF GENERAL APPLICABILITY FOR THE DETERMINATION OF COMBINED SULPHURIC ACID.

By Launcelot W. Andrews.

Of the volumetric methods at present in use for the determination of sulphuric acid, none can be considered entirely satisfactory, although some of them are very useful for technical purposes. Several of these methods involve a double titration, some require three standard solutions,[1] and others are only applicable in the absence of bases precipitable by sodium carbonate.

The author believes, therefore, that the presentation of a new method, applicable in the presence of magnesium, calcium, alumi-

[1] Precht, Ztschr. anal. Chem., 1879, 521.

num, zinc, manganese, iron (ferric), nickel, cobalt, and silver, which requires but one standard solution with a single titration, and which in precision is at least equal to the ordinary gravimetric determination as barium sulphate, while demanding much less time for its execution, will not be thought superfluous.

The process depends upon the following series of reactions: First, to the solution of a sulphate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralised with ammonia or calcium carbonate, and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulphate solution (1 cc. = 12.654 mg. iodine = 2.662 mg. SO_3).

The barium chromate employed may contain barium sulphate, but must be completely freed from soluble chromates and from barium carbonate, nitrate or chloride, by prolonged washing, first with boiling water slightly acidified with acetic acid, finally with hot distilled water, until the washings give no precipitate with sulphuric acid, and (in a quantity of 100 cc.) a barely perceptible reaction with hydrochloric acid, potassium iodide and starch paste.[1]

A suitable solution of the barium chromate is prepared by digesting it with hydrochloric acid containing 36 grams acid in the litre. This solution will contain from 2 to 4 per cent. of barium chromate, according to the temperature at which it was prepared.

The reagent being ready, the analysis is performed as follows:

The sulphate to be determined is diluted, if necessary, until it does not contain more than 2 per cent., at most, of sulphuric anhydride, is made approximately neutral, and is heated to boiling. While boiling hot, an excess of the barium chromate solution is gradually introduced, and the boiling continued one minute, or longer, if carbonates were present.

The precipitate of barium sulphate is always yellow from the barium chromate which it carries down with it, provided sufficient excess of the latter reagent was added.

Calcium carbonate, which must be entirely free from barium or strontium carbonates or calcium sulphate, is then thrown in small portions into the still hot liquid until no further evolution of carbonic anhydride is observed, and the boiling continued one or two minutes. The solution is filtered while hot, and the precipitate is washed with a small quantity of hot water until the washings are colorless, and a little longer. Under these conditions the barium chromate has no tendency to run through the filter or to retain any soluble chromate. 75 cc. of water will usually be found more than sufficient to effect the washing.

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[1] When barium chloride is precipitated with an excess of potassium chromate, the water with which the precipitate is washed will, for a long time, show a yellow color. This is not, as has been supposed, due to the solubility of $BaCrO_4$, but to the fact that it obstinately retains soluble chromate. According to the author's observations, barium chromate is not sufficiently soluble in water to impart any color to the latter. According to the mean of four concordant determinations, one million parts of water dissolve 15 parts barium chromate at 18°.4 C.

If, on the other hand, the solution is allowed to stand over night with the precipitate in it, calcium chromate will be retained and a longer washing becomes necessary. In this case the results may come somewhat too high, in consequence of the necessarily large amount of wash-water dissolving an appreciable quantity of barium chromate. Under normal conditions the error from this source is quite insignificant.

The filtrate, after cooling, is treated with a sufficient amount of crystals of potassium iodide (free from iodate) and with 5 to 7 cc. fuming hydrochloric acid for each 100 cc. of liquid. This amount of acid is enough to induce a prompt and complete reduction of the chromate, but not enough to decompose the starch paste. It is advisable to run in the decinormal sodium thiosulphate from a burette until the brown color of the iodine is nearly discharged before adding the starch, and then to continue the titration slowly, with constant stirring, until the turning point is reached.

The above process must be modified in the presence of ferric, nickel, or zinc salts by using ammonia instead of calcium carbonate to neutralise the acid liquid. The solution in this case is to be made distinctly alkaline, and the excess of ammonia boiled nearly away before filtering. The necessity for this modification arises from the fact that if a ferric or nickel or zinc salt is boiled with a chromate and calcium carbonate, basic chromates of iron and nickel are precipitated, from which the chromic acid cannot be removed, or only with difficulty, by washing. Barium chromate, when precipitated from its acid solution by ammonia, does not possess the agreeable properties which it shows when thrown down by calcium carbonate. It is much more finely divided than in the latter case, tends to run through the filter, which must therefore be double or of very dense paper, and requires a longer washing to remove the soluble chromates which it more tenaciously retains; consequently, ammonia is only to be used when the employment of calcium carbonate is inadmissible. It is not practicable to precipitate the excess of barium chromate with sodium acetate from hydrochloric acid solution. Numerous experiments, the details of which it is not worth while to give, show that barium chromate is so soluble in hot dilute acetic acid[1] that the results fall 3 to 5 per cent. too high, while if precipitated cold and allowed to stand, the results are too low.[2]

The following analyses show the applicability of the method:

I. Taken 10 cc. of a solution containing 20.8984 grams pure and dry ammonium sulphate per litre. Diluted to 50 cc., treated with 15 cc. $BaCrO_4$ solution and with $CaCO_3$, as described above.

Required 47.60 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol. $=$ .1267 gram SO_3 found. Calculated, .1266 gram SO_3; 100.08 per cent. found.

II. Taken 10 cc. of the same ammonium sulphate solution and treated as in No. I. Required 47.60 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol.

The volume of the solution before titration was 300 cc. 100.08 per cent. found.

III. 20 cc. of the same ammonium sulphate solution, treated as before, required 95.50 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol.

Total volume of the solution, 400 cc.; 100.37 per cent. found.

IV. Taken .2980 gram $CuSO_4 + 5H_2O$, small crystals obtained by triple recrystallisation of a commercial sample. The copper was precipitated from boiling sol. with $(NH_4)_2S$ (free from sulphate), solution boiled with acetic acid to expel H_2S, filtered and filtrate treated as above.

35.95 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol. required $=$ .0957 gram $SO_3 =$ 32.11 per cent. found. Theoretical per cent. $=$ 32.09.

V. Taken 10 cc. $(NH_4)_2SO_4$ solution (see I) containing .20898 gram, diluted to 100 cc., treated with 20 cc. $BaCrO_4$ sol. as above and neutralised with ammonia. Required 47.30 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol. $=$ .1260 gram SO_3 instead of .1266 gram. Found 99.52 per cent.

VI. Taken .6485 gram $(NH_4)_2Fe_2(SO_4)_4 + 24H_2O$. Treated as No. V. Required 80.65 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol. $=$ .2147 gram SO_3. Calculated .2153 gram SO_3. Found 33.11 per cent. SO_3. Theory 33.20 per cent.

VII. *a.* Taken 100 cc. of the Iowa City water supply. Treated as No. V. Required 2.10 cc. $\frac{1}{10}$ $Na_2S_2O_3$. sol.

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[1] Compare Morse, this Journal 2, 176.

[2] The method cannot be used in the presence of phosphoric acid, and, of course, all reducing agents, as well as bismuth and copper salts, must be excluded.

b. Taken 200 cc. ditto, ditto. Required 4.30 cc. $\frac{1}{10}$ $Na_2S_2O_3$ sol. Found 56 mg. and 57 mg. SO_3 per litre. A gravimetric analysis gave 58 mg. SO_3 per litre.

It seems probable that an indirect determination of sodium and potassium would be possible by weighing these elements as sulphates and determining the sulphuric anhydride volumetrically as described. Experiments to test this are now in progress. If feasible, it is evident that it would often be more convenient than the usual indirect determination as chlorides, while free from some of the well known sources of error involved in the gravimetric determination of sulphuric acid in the presence of alkalies.

It is both a duty and a pleasure for me to take this opportunity to express publicly my thanks to Mr. F. W. Spanutius, instructor in chemistry here, for the zeal and skill with which he has assisted me in the experimental part of this investigation. Some of the test analyses given above were performed by him.

THE UNIVERSITY OF IOWA, *November* 16, 1889.

REVIEWS AND REPORTS.

ON THE NATURE OF TELLURIUM.[1]

The atomic weight of tellurium, as determined thus far, appears to be greater than that of iodine, though the results obtained by different investigators vary between wide limits. Berzelius found 128.9 and 128.3, v. Hauer 127.9, and Wills 126.39–129.66. ($O = 16$ is used as the standard throughout the paper.) But from the arrangement of the elements according to the periodic system we should expect tellurium to fall in the same family as sulphur and selenium, and therefore to have an atomic weight of about 123.5, lying between that of antimony (119.96) and that of iodine (126.86). The author undertook the present investigation in order to make a thorough revision of the atomic weight of tellurium. The tellurium used was prepared from various Hungarian ores and from Hungarian crude tellurium, being carefully purified in each case, and finally distilled in a current of hydrogen. The element as thus obtained possessed the properties required of pure tellurium according to the present state of our knowledge.

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[1] Abstract of a paper by B. Brauner: Chem. Soc. Journ. 1889, 382.

Many different methods were tried for the determination of the atomic weight. Several of these were, however, abandoned on account of the great experimental difficulties encountered. Three of the methods involved the synthesis of a telluride (of copper, silver, or gold), but it was found impossible to obtain these compounds in pure condition on account of the tendency of the metals to take up an excess of tellurium which could scarcely be driven off at a yellow heat.

The results which the author considers reliable were obtained by the methods described below.

1. *Oxidation of tellurium with aqua regia.*—Weighed quantities of tellurium were treated with nitrohydrochloric acid and the solution was evaporated to dryness, care being taken to prevent the escape of any tellurium tetrachloride which might be volatilised. The residue was then evaporated several times with nitric acid and finally heated to 440°. The resulting dioxide was weighed. Five experiments gave $Te = 125.0–126.4$. It was observed that when the tellurium dioxide was treated, after weighing, with hydrochloric acid, a *white insoluble residue* was always left.

2. *Conversion of tellurium dioxide into the basic sulphate.*—The dioxide was treated with hydrochloric acid, and the solution (always containing some undissolved white substance) was evaporated to dryness with a slight excess of sulphuric acid. Crystals of the basic sulphate $Te_2O_4SO_3$ were thus obtained. Three experiments gave $Te = 125.0–127.5$.

3. *Conversion of tellurium into the basic sulphate.*—The tellurium was weighed as such, converted into the dioxide, and the dioxide then converted into the basic sulphate. Six experiments gave $Te = 124.6–127.1$.

4. *Analysis of tellurium tetrabromide.*—The tetrabromide was prepared by adding powdered tellurium to pure bromine, and then removing the excess of bromine by warming the mixture and passing through it a current of dry carbon dioxide. The product was found to contain some tellurium which had been protected from the action of the bromine. On heating together tellurium and tellurium tetrabromide, the dibromide is formed, thus: $TeBr_4 + Te = 2TeBr_2$. It was found possible to separate the dibromide from the tetrabromide by fractional sublimation in a vacuum, the dibromide being entirely volatilised and driven out of the tube at 200°. On afterwards raising the temperature to about 300° the tetrabromide sublimed. A weighed quantity of this tetrabromide was dissolved in a solution of tartaric acid, and the bromine then precipitated as silver bromide with certain special precautions. One experiment gave (after the method had been perfected) $Te = 127.61$.

The results obtained by the methods above described varied so greatly that the author was led to attempt to decompose tellurium by several methods of fractionation.

First method.—Tellurium tetrabromide was sublimed as before, but in two portions. The percentage of bromine was then estimated by a combined gravimetric and volumetric method, which was found to give excellent results. The amount of silver necessary for each precipitation was calculated, accurately weighed, and dissolved in nitric acid. After adding the silver nitrate to the tartaric acid solution of the tetrabromide, the resulting precipitate was agitated for many hours in the dark to rid it from the impurities which it held. After clearing the liquid, the *very small* excess of silver or bromine present was estimated by standard decinormal solutions. The more volatile portion gave Te = 127.60 and 127.63, while the less volatile portion gave Te = 127.59 and 127.63. These results, as will be seen, agree perfectly with that obtained before by the simple gravimetric method.

Second method.—Crude tellurium after being dissolved was precipitated by sulphurous acid. It was then fused with potassium cyanide, dissolved, and precipitated fractionally by a current of air. Each portion was then distilled separately in a current of hydrogen, converted into the tetrabromide and analysed as before.

Fraction No. I gave Te = 127.67 and 127.67.
Fraction No. II gave Te = 127.60.
Fraction No. IV gave Te = 127.64 and 127.67.

Third method.—A hydrochloric acid solution of pure tellurium dioxide was precipitated fractionally with ammonia (fractions I–VIII) and then with sulphurous acid (fraction IX). Each fraction was then converted into the tetrabromide and analysed.

Fraction No. I gave Te = 127.60.
Fraction No. IV gave Te = 127.71.
Fraction No. IX gave Te = 127.57.

The different fractions as obtained by these three methods seem identical.

Tellurium tetrabromide was then prepared from tellurium which had been carefully purified and finally fused in a current of hydrogen, but not distilled. The tetrabromide was separated from the dibromide by subliming the latter in a vacuum, but was not itself sublimed, being found to decompose. Its color was greenish, while the tetrabromide made from tellurium which has been *distilled* in a current of hydrogen has an orange color. Three analyses gave Te = 129.63, 137.72, and 128.88.

The results show that "if tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained."

5. *Analysis of tellurium dibromide.*—The dibromide was prepared by fusion of the tetrabromide with an excess of tellurium and subsequent sublimation in a vacuum. Its appearance under different conditions seems to show that it is a mixture either of several allotropic modifications or of different substances. The bromine was estimated gravimetrically. Four experiments gave Te = 130–133.

From the widely divergent results obtained by these different methods for the determination of the atomic weight the author concludes that *tellurium is not a simple substance.*

The difference in composition and properties between the tetrabromide prepared from tellurium distilled in a current of hydrogen and that prepared from tellurium which has not been distilled, makes it appear very probable that one constituent of tellurium escapes, partly, during the distillation.

Having found it necessary to prepare pure silver for use in these researches, the author undertook to determine the amount of oxygen occluded by the metal when obtained by one of the methods of Stas. The silver after precipitation with ammonium sulphite and digestion with ammonia, was fused with borax and nitre, and poured into a mould of kaolin, the bars thus formed being afterward carefully freed from any external impurity.

Silver prepared in this way was heated nearly to its melting point and allowed to cool. It was then placed in a combustion tube, heated to 150°, and pure dry air drawn over it for some time. One end of the tube was then sealed and the air exhausted by a Sprengel pump. After standing over night it was again exhausted, and when a vacuum as perfect as possible was obtained, the tube containing the silver was heated to 450°, the pump acting all the time, and the gas given off being collected. A red heat was then applied, and the tube was pumped out at this temperature for six hours. 153.2133 grams of silver were used.

Up to 450° there was given off .219 cc. of gas (reduced to normal conditions). Above 450° there was given off .844 cc. of gas. This was analysed by means of microeudiometers, and found to consist of .586 cc. of oxygen and .298 cc. of nitrogen. Now, .298 cc. of nitrogen corresponds to .312 cc. of air, so that the amount of oxygen given up above 450° was .532 cc.

A similar experiment using no silver gave .249 cc. of gas collected. Another experiment was made, using the silver of the previous experiment. In this case the silver was allowed to cool in a vacuum, then heated to 150°, and air drawn over it. This, when heated again to redness in a vacuum, gave .215 cc. of gas (air) collected. Now, .249 and .215 are practically identical with .219, the amount obtained up to 450° in the first experiment, and this is therefore to be neglected.

The experiments show that 153.2133 grams of silver heated to redness in a Sprengel vacuum give off .312 cc. of air (probably condensed) and .532 cc. of oxygen, so that the composition of the metal used was

Silver, ...	99.9995
Oxygen, ...	.0005
	100.0000

As the very slight impurities of the undistilled silver of Stas, .003–.006 per cent., were not regarded by him, it is evident that his researches "do not require the correction proposed by Dumas, due to an occlusion of oxygen in silver, its quantity being practically nought." C. E. SAUNDERS.

THE CONDITION OF MATTER IN THE VICINITY OF THE CRITICAL POINT.

A communication by Cailletet and Colardeau in reference to this subject has recently been published.[1] They have made some interesting investigations, and the conclusions deduced therefrom may prove of considerable importance, especially in the problem of the liquefaction of gases.

In 1822 Cagniard de La Tour observed that when liquids are heated in sealed tubes, the surface of demarcation between liquid and gas disappears at a certain temperature, which differs with the liquid used.[2] He inferred that, at that temperature, the liquid is completely converted into vapor in the space in which it is confined. In accordance with this view, the critical temperature would be that at which a sudden discontinuity is occasioned—the temperature above which the liquid state ceases to exist. But Ramsay, in 1880, expressed the opinion that the liquid state continues above the critical temperature; and it is to this matter that the attention of Cailletet and Colardeau is first directed. The following experiment, described by them, tends to confirm Ramsay's opinion. A small quantity of iodine is deposited, by vaporisation, in the upper part of a tube used for compression of carbon dioxide. As soon as the carbon dioxide that has been liquefied attains such a level as to come in contact with the iodine, it assumes a color similar to the color of a solution of iodine in chloroform, while the gaseous carbon dioxide above, though in contact with the solid iodine on the walls of the tube, remains perfectly colorless. Now, on heating the tube above 31° (the critical temperature of carbon dioxide), the meniscus disappears; the color, however, is not diffused through the entire length of the tube, but remains just where it was before—that is, in that portion of the tube occupied by the liquid carbon dioxide before the tube was heated. In the vicinity of the place from which the meniscus has disappeared the color is gradually less distinct, but the upper

[1] Ann. chim. phys. (6) **17**, 269.

[2] Ibid. (2) **21**, 127.

part of the tube remains perfectly colorless. This seems to indicate that only the surface of the liquid has disappeared, and that the liquid continues to exist, as such, in the lower part of the tube. Spectroscopic examination indicates that, after the critical temperature is reached, the iodine is still dissolved in a liquid, and not in a gas.

The following facts lead to the same conclusion as the above. Let a tube partly filled with liquid carbon dioxide be heated to and above the critical temperature of the same. The pressure increases with the temperature, and, with the data thus obtained, a curve can be traced which will represent the gradual change in tension of the vapor as the temperature rises. Now, it is found that such a curve above the critical temperature is simply a prolongation of the curve below the critical temperature. But, if at the critical temperature total vaporisation had taken place, then, starting at this temperature, the vapor would no longer have been saturated, and the curve representing its expansion would not be a prolongation of the curve of saturated vapor. Furthermore, if several similar experiments be made, using in each case the same tube but different quantities of liquid carbon dioxide, the curves traced will cease to be identical as soon as the critical temperature is attained. This, also, shows that the liquid state must continue beyond the critical temperature. It is evident that if the liquid had been completely vaporised at this temperature, the curves would in each case continue to be identical. On the other hand, if the liquid state continued, vaporisation continued beyond the critical temperature; the vapor was still saturated, and hence the greater the quantity of liquid remaining in the tube at the critical temperature, the more rapidly would the tension increase after this temperature was attained. In consequence of this, the curves would cease to be identical just at the critical temperature.

A few years ago Jamin offered the following hypothesis as an explanation of the conduct of a liquid when heated in a sealed tube. As the temperature rises, the density of the liquid diminishes by reason of its expansion; meanwhile, the quantity of superposed vapor rapidly increases, and its density increases. At a certain temperature the density of liquid and vapor must become equal. Just at this temperature the surface of demarcation becomes indistinct, and the liquid, having lost all its weight, floats in an atmosphere of the same density, forming with it a genuine emulsion. Now, on continuing to heat the tube after the disappearance of the meniscus, the density of the liquid must continue to decrease and that of the vapor to increase. The density of the vapor will become greater than that of the liquid, and a phenomenon just the reverse of the above should be observed, that is to say, the liquid should collect in the upper part of the tube and the gas in the lower part. This second part of Jamin's hypothesis has been the occasion of numerous experiments, but the results have always been negative, although the temperature has been raised to such an extent as to cause fracture of the tubes.

An experiment by Cailletet and Colardeau occasioned serious doubt in regard to Jamin's hypothesis. This was followed by another experiment which seems quite conclusive as to this matter, and may be described as follows: In the two branches of an O-tube which contains a quantity of sulphuric acid more than sufficient to fill the lower curvature, carbon dioxide is compressed. The height of the sulphuric acid in the two branches of the tube is the same. On cooling one branch of the tube, the greater part of the carbon dioxide condenses to a liquid in that branch, while a portion condenses in the other branch. Under these conditions there is a considerable depression of the level of the sulphuric acid in that branch which contains the larger quantity of liquid carbon dioxide. When the tube is gradually heated in a bath of tepid water the difference in height of the sulphuric acid in the two branches diminishes somewhat, but even at the critical temperature this difference does not by any means entirely disappear, as would have been the case if, at that temperature, the density of the liquid had become equal to that of the superposed vapor. This experiment also proves that the critical temperature is not, as Cagniard de La Tour supposed, that temperature at which total vaporisation takes place; for, if this were true, the height of the sulphuric acid at the critical temperature would, of course, have been the same in both branches of the tube. When the tube was cooled it was observed that more carbon dioxide condensed to a liquid in that branch in which more of the liquid was previously contained, an additional proof of the continuation of the liquid state above the critical temperature.

Cailletet and Colardeau draw the following conclusions from their investigations: 1. The critical temperature of a liquid is not that temperature at which the liquid suddenly and completely vaporises in the space in which it is confined. The liquid state continues above that temperature. 2. It is not that temperature at which the liquid and its saturated vapor have the same density. 3. It is that temperature at which the liquid and the gaseous atmosphere above it become susceptible of mutual solution in all proportions, forming, after agitation, a homogeneous mixture. This conclusion applies to the critical point as observed by increase of pressure on mixtures partially liquefiable (such, for example, as mixtures of carbon dioxide and air), as well as to that observed by the elevation of the temperature of a liquid.

Since the liquid state continues above the critical temperature, it follows that, in order to liquefy a gas, it is not absolutely necessary to reduce the temperature lower than its critical temperature. When the pressure is sufficient, liquefaction must take place above this temperature, the liquid dissolving in the still non-liquefied gaseous mass. In the case of carbon dioxide this has been verified by Cailletet and Colardeau. Under a pressure of 80 to 100 atmospheres, and at a temperature about 9° above its critical temperature, liquefaction took place, as was indicated by solution of some iodine that had been deposited in the tube in which the experiment was performed.

When a liquid contained in a sealed tube is heated to its critical temperature, the meniscus, just prior to its disappearance, seems to grow thicker and to diffuse itself. Soon, however, the contents of the tube become apparently homogeneous. Now, on cooling, a little cloud is observed in the same part of the tube, which vanishes as the meniscus reappears. These phenomena Cailletet and Colardeau attribute to the reciprocal solution of gas and liquid in the neighborhood of the surface of demarcation. Just at this moment the tube contains all possible transitions from a perfect liquid at the base to a perfect gas at the summit.

C. C. BLACKSHEAR.

THE REACTIONS OF HYDROGEN PEROXIDE WITH CHROMIC ACID AND THE CHROMATES.

In the September (1889) number of the *Annales de Chimie et de Physique*, M. Berthelot reports his investigations upon the above subject. A brief abstract of his paper is here given.

Barreswil was the first to call attention to the blue coloration produced by the action of hydrogen peroxide upon potassium bichromate and gave the name of "perchromic acid" to the blue substance soluble in ether. He believed its composition to be represented by a symbol which would now be written $HCrO_4$. Moisson concluded that the substance is a compound of chromic acid and hydrogen peroxide; M. Berthelot, that it is a compound of perchromic acid and hydrogen peroxide.

When potassium permanganate and hydrogen peroxide are brought together, each loses the same amount of oxygen; it makes no difference whether the peroxide be added to the permanganate, or *vice versa*. In the case of hydrogen peroxide and potassium bichromate, on the other hand, the character of the reaction depends upon which of the two substances is in excess. If the peroxide is added to the mixture of bichromate and hydrochloric or sulphuric acid, and the solutions are extremely dilute, scarcely a trace of perchromic acid is formed, and the peroxide and bichromate, in being simultaneously reduced, lose equal quantities of oxygen. If, on the contrary, the bichromate is added to the peroxide—the latter being thus in excess—the blue coloration is noticed, and the amount of peroxide decomposed by a given quantity of bichromate is greater than when the operation is conducted in the former way—the ratio between the amounts of oxygen lost by the peroxide and bichromate being 1.52–1.63:1. These results were the same whether hydrochloric or sulphuric acid is used, and whether the acid is mixed with the bichromate or with the peroxide. The quantity of acid taken was just that amount necessary to convert the products of the reduction of the bichromate into potassium and chromium chloride or sulphate. If nitric acid is used the evolution of oxygen is more rapid, but the result is practically the same.

If in adding the peroxide to the excess of bichromate, or the bichromate to the excess of peroxide, care is not taken to have the solutions very dilute and to add very slowly, there will be an excess of the *added solution* at certain points, and here the reaction will take place in a different way from the main reaction. The variation in the relative quantities of oxygen given off (as given above) is probably due to this condition.

Following M. Berthelot's reasoning, it appears probable that, when the peroxide is added to the bichromate in excess, the reaction is represented by the following equations:

(*a*) $K_2Cr_2O_7 + 8HCl + 3H_2O_2 = 2KCl + 2CrCl_3 + 4H_2O + 3H_2O_3$,
and (*b*) $3H_2O_3 = 3H_2O + 3O_2$.

Combining (*a*) and (*b*), we have

I. $K_2Cr_2O_7 + 8HCl + 3H_2O_2 = 2KCl + 2CrCl_3 + 7H_2O + 3O_2$.

When the bichromate is added to the peroxide in excess the reaction is supposed to take place thus:

(*a*) $K_2Cr_2O_7 + 2HCl + H_2O_2 = 2KCl + 2HCrO_4 + H_2O$,
(*b*) $2HCrO_4 + 4H_2O_2 + 6HCl = 2CrCl_3 + 4H_2O + 4H_2O_3$, and
(*c*) $4H_2O_3 = 4H_2O + 4O_2$.

Combining (*a*), (*b*) and (*c*), we have

II. $K_2Cr_2O_7 + 8HCl + 5H_2O_2 = 2KCl + 2CrCl_3 + 9H_2O + 4O_2$.

On comparing equations I and II it will be noticed that the ratio between the quantities of peroxide decomposed by a given quantity of bichromate = 3:5 or 1:1.66, which is near the figure obtained by M. Berthelot in actual experiment. The variation is probably due, as stated above, to the fact that at some points the reaction took place according to equation I, while the principal decomposition was that represented by equation II. A calorimetric determination showed that when the peroxide is added to the bichromate the heat evolved is 45.2 cal.; when the bichromate is added to the peroxide, 66.8 cal.

When a very weak acid, such as boric or hydrocyanic acid, is used instead of one of the strong mineral acids, a brown coloration is produced, which at once changes to blue on adding sulphuric acid. Such acids as phosphoric and acetic give the blue color, sometimes mixed with the brown, yielding, however, the blue color alone on addition of sulphuric acid. This brown color M. Berthelot believes to be due to the formation of a compound of chromium chromate and hydrogen peroxide. If an extremely dilute solution of pure chromic acid is treated with hydrogen peroxide the brown color alone is noticed.

When hydrogen peroxide is brought together with pure potassium bichromate the color changes to an intense brown, then effervescence begins, and finally the solution slowly assumes again its original color. A fresh addition of peroxide produces the same effects as the first—the bichromate is left undecomposed, the solution containing at the end of the experiment no trace of perchromic acid or of chromic salt. Pure potassium chromate decomposes hydrogen peroxide, though more slowly than the bichromate, the salt being found unchanged at the end of the experiment. In order to ascertain whether the decomposition of the peroxide is due to the formation of an intermediate product, M. Berthelot brought together solutions of the peroxide and bichromate and, while the reaction was in progress, added dilute ammonia. A precipitate consisting of chromic oxide, ammonium chromate and hydrogen peroxide was thrown down. The supernatant solution was decanted off and the precipitate repeatedly washed with pure water. The precipitate decomposed rapidly, however, coloring the wash-liquor yellow and giving off bubbles of oxygen. The presence of each of the three constituents was nevertheless proved. The action would, therefore, seem to consist in the formation of an unstable compound through the simultaneous reduction of the peroxide and the bichromate, and in the reformation of the bichromate with the reduction of still more peroxide. If pure chromic oxide, in the presence of potash, is treated in the cold with hydrogen peroxide, a precipitate similar to that described is formed and this decomposes with the formation of potassium chromate. In the presence of ammonia the same kind of transformation takes place, the action, however, being extremely slow in cold solution.

W. W. RANDALL.

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